

JC18 Rec'd PCT/PTO 19 OCT 2001

Atty. Docket #: 0732/990023  
(Basell-5)**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

---

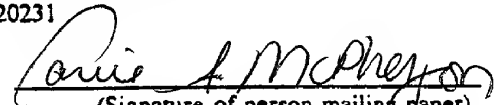
**INTERNATIONAL APPL. NO.:** PCT/EP00/03263 :**INTERNATIONAL FILING DATE:** -04/12/2000- :**APPLICANT:** JÖRG SCHOTTEK ET AL :**SERIAL NO:** (To be assigned) : **ART UNIT:****FILED:** -HEREWITH- : **EXAMINER:****FOR:** "CATALYST SYSTEM" :  
:

---

**Commissioner for Patents**  
**Box PCT**  
**Washington, D.C. 20231****\*Express Mail\* No.:** ET481431579**Date:** -OCTOBER 19, 2001-

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

-Carrie A. McPherson-  
(Typed or printed name of mailing paper or fee)

  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS**  
**TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)**  
**CONCERNING A FILING UNDER 35 U.S.C. §371**  
**(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

0732/990023  
(Base11-5)

International Application No. PCT/EP00/03263

0732/990023  
(Base11-5)

9. ☒ An <sup>unexecuted</sup> oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) is enclosed  
☒ and is attached to the translation of (or a copy of) the International Application.  
☐ and is attached to the substitute specification.

10. ☐ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.  
12. ☒ An Assignment is enclosed for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.  
13. ☒ A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.  
14. ☐ A substitute specification (including claims, abstract, drawing) is enclosed.  
15. ☐ A change of power of attorney and/or address letter is enclosed.  
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

☐ 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☐ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP00/03263

0732/990023  
(Base11-5)

- ☒ Receiving Office: EPO  
☒ IPEA (if filing under 37 CFR 1.495): EPO  
☒ Priority Claim(s) (35 USC §§ 119, 365):  
German Appln. 199 17 985.9 filed -April 21, 1999-.  
☒ A copy of the International Search Report is

☐ enclosed.

☐ attached to the copy of the International  
Application.

- ☒ A copy of the Receiving Office Request Form is enclosed.

- ☒ Form PTO/SB/05 (1) sheet  
☒ Form PCT/IB/306 (1) sheet  
☒ Form PCT/IPEA/409 (5) pages In German  
☒ AMENDED SHEETS pps. 59-60 (Claims 1-4)  
☒ Form PCT/ISA/220 (7) pages including search report

The fee calculation is set forth on the next page of this Transmittal Letter.

JG13 Rec'd PCT/PTO 19 OCT 2001

# FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 890.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$84..... -0-

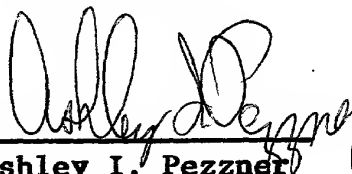
Fee for multiple dependent  
claims \$280..... -0-

TOTAL FILING FEE... \$ 890.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

Ashley I. Pezzner  
Reg. No. 35,646  
CONNOLLY BOVE LODGE & HUTZ LLP  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

AIP/cam  
Enclosures

F:\docs\fori\40975 = F:\docs\patn\56657.doc  
(9086\*179-Base11-5)

ATTORNEY DOCKET NO.: BASELL-5 (9086\*179)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: JÖRG SCHOTTEK *ET AL.* )  
SERIAL NO. TO BE ASSIGNED ) ART UNIT: TO BE ASSIGNED  
FILED: HEREWITH ) EXAMINER: TO BE ASSIGNED  
FOR: CATALYST SYSTEM )

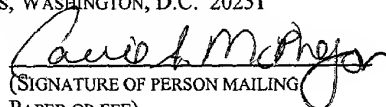
Asst. Commissioner for Patents

Washington, D.C. 20231

"EXPRESS MAIL" No. ET481431579 DATE: OCTOBER 19, 2001

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON  
(TYPED OR PRINTED NAME OF  
PERSON MAILING PAPER OR FEE)

  
(SIGNATURE OF PERSON MAILING  
PAPER OR FEE)

**PRELIMINARY AMENDMENT**

Sir:

Prior to fee calculation and examination please amend the above-identified application as follows.

**In the Specification**

Please delete the paragraph at page 1, lines 39-42 and insert the following:

- - US-A 5,384,299 describes zwitterionic catalyst systems prepared by protolysis from dialkyl-metallocene compounds and salts of the formula  $[R_3NH]^+ [B(C_6F_5)_4]^-$ . C-H Activation as subsequent reaction does not occur here. - -

See Appendix I for the changes. The term underlined was added to the specification and the term bracketed was canceled from the specification.

**In the Claims**

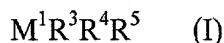
09980926 . 01.10.01

Please cancel claims 1-4.

Please add the following new claims.

- 5. A catalyst system comprising

- A) at least one metallocene,
- B) at least one Lewis base of the formula I



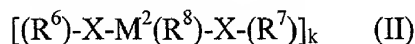
wherein

$R^3$ ,  $R^4$  and  $R^5$  are identical or different and are each a hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_6$ - $C_{40}$ -haloaryl,  $C_7$ - $C_{40}$ -alkylaryl or  $C_7$ - $C_{40}$ -arylalkyl group or two or all three of the radicals  $R^3$ ,  $R^4$  and  $R^5$  may be joined to one another via  $C_2$ - $C_{20}$  units,

$M^1$  is an element of main group V of the Periodic Table of the Elements,

C) at least one support,

D) and at least one organoboron or organoaluminum compound which is made up of units of the formula II



wherein

$R^6$  and  $R^7$  are identical or different and are each a hydrogen atom, a halogen atom, a boron-free  $C_1$ - $C_{40}$  group or an  $Si(R^9)_3$  group,

where  $R^9$  is a boron-free  $C_1$ - $C_{40}$  group,

$R^8$  can be identical to or different from  $R^6$  and  $R^7$  and is a hydrogen atom, a halogen atom, a  $C_1$ - $C_{40}$  group or an  $OSi(R^9)_3$  group,

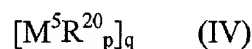
X may be identical or different and are each an element of group V or VIa of the Periodic Table of the Elements or an NH group,

$M^2$  is an element of group IIIa of the Periodic Table of the Elements and

$k$  is a natural number from 1 to 100,

and is covalently bound to the support.

6. The catalyst system as claimed in claim 5, which further comprises an organometallic compound of the formula (IV)



wherein

$M^5$  is an element of main group I, II or III of the Periodic Table of the Elements,

$R^{20}$  are identical or different and are each a hydrogen atom, a halogen atom or a  $C_1$ - $C_{40}$  group,

$p$  is an integer from 1 to 3 and

$q$  is an integer from 1 to 4.

7. The catalyst system as claimed in claim 5, wherein  $M^1$  is nitrogen or phosphorus.
8. The catalyst system as claimed in claim 7,

wherein

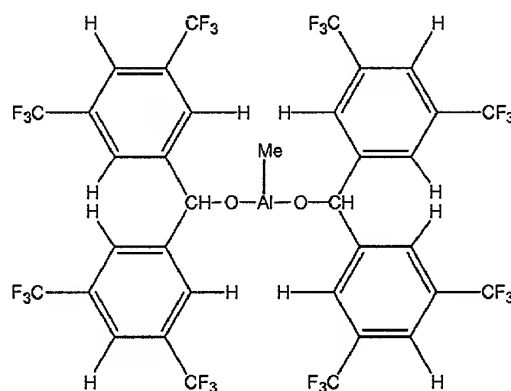
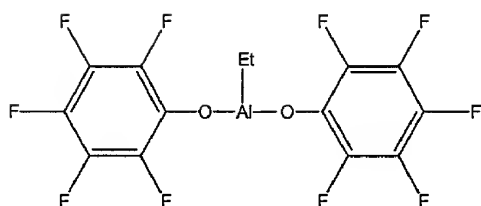
$R^6$  and  $R^7$  are identical or different and are each a hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl or an  $Si(R^9)_3$  group,

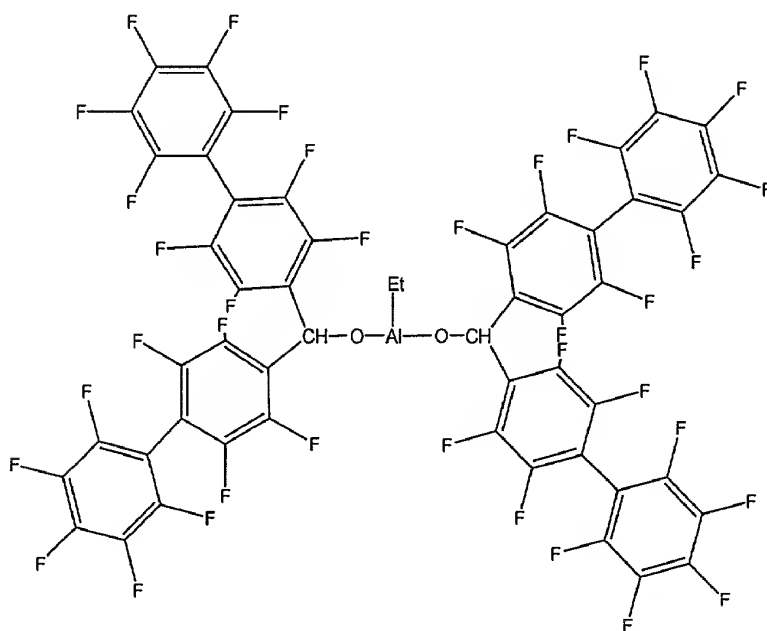
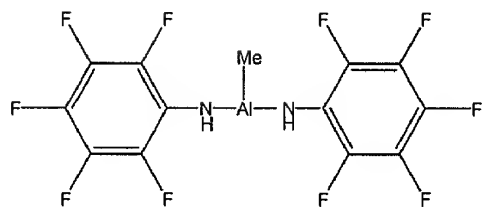
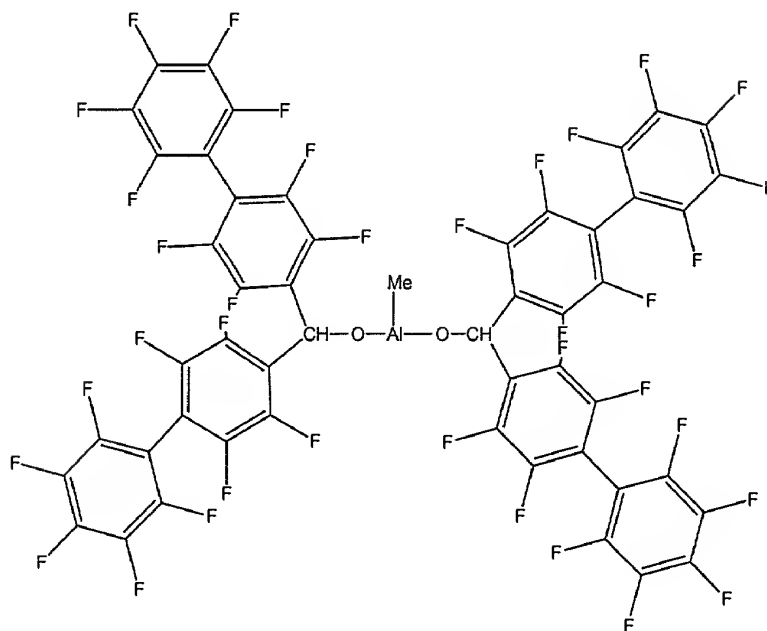
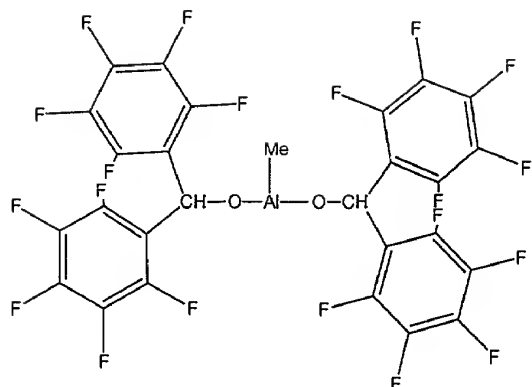
$R^9$  is a  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl,

$R^8$  is a hydrogen atom, a halogen atom,  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl or an  $OSi(R^9)_3$  group.

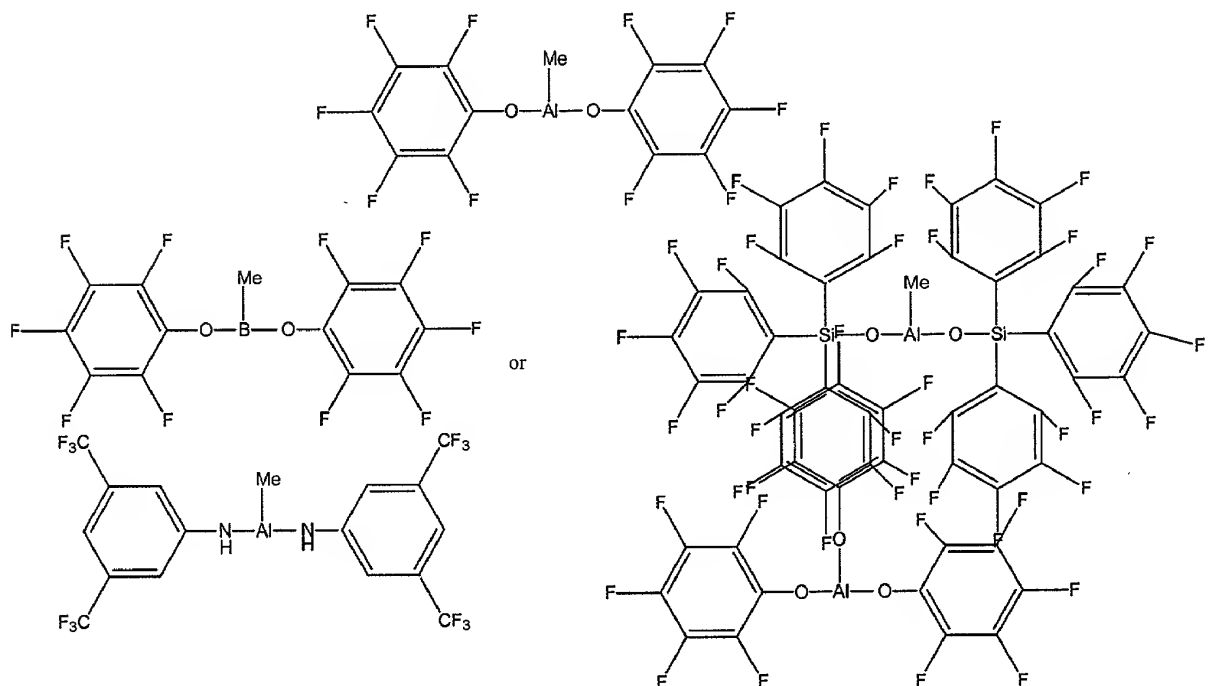


9. The catalyst system as claimed in claim 5, wherein the compound of the formula II is selected from the group consisting of



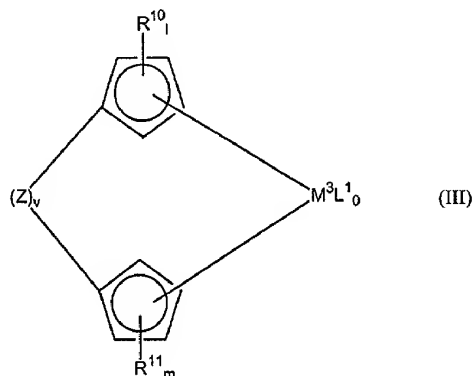


10. The catalyst system as claimed in claim 5, wherein the compound of the formula II is



11. The catalyst system as claimed in claim 8, wherein  $\text{M}^2$  is boron.
12. The catalyst system as claimed in claim 5, wherein  $\text{R}^8$  is hydrogen atom, a halogen atom, a  $\text{C}_2\text{-C}_{20}$ -alkyl,  $\text{C}_1\text{-C}_{20}$ -haloalkyl,  $\text{C}_1\text{-C}_{10}$ -alkoxy,  $\text{C}_6\text{-C}_{20}$ -aryl,  $\text{C}_6\text{-C}_{20}$ -haloaryl,  $\text{C}_6\text{-C}_{20}$ -aryloxy,  $\text{C}_7\text{-C}_{40}$ -arylalkyl,  $\text{C}_7\text{-C}_{40}$ -haloarylalkyl,  $\text{C}_7\text{-C}_{40}$ -alkylaryl,  $\text{C}_7\text{-C}_{40}$ -haloalkylaryl or an  $\text{OSi}(\text{R}^9)_3$  group.
13. The catalyst system as claimed in claim 9, wherein said at least one support is talc, an inorganic oxide or a polymer powder.
14. The catalyst system as claimed in claim 5, wherein said at least one support is talc, polyolefin powder,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , aluminum oxide or  $\text{B}_2\text{O}_3$ .

15. The catalyst system as claimed in claim 6, wherein  $M^5$  is lithium or aluminum and  $R^{20}$  are identical or different in each area hydrogen atom, a halogen atom, a  $C_1$ - $C_{20}$ -alkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -arylalkyl or  $C_7$ - $C_{40}$ -alkylaryl.
16. The catalyst system as claimed in claim 10, which further comprises a trimethylaluminum, triethylaluminum, triisopropylaluminum, trihexylaluminum, trioctylaluminum, tri-n-butylaluminum, tri-n-propylaluminum, triisoprenylaluminum, dimethylaluminum monochloride, diethylaluminum monochloride, diisobutylaluminum monochloride, methylaluminum sesquichloride, ethylaluminum sesquichloride, dimethylaluminum hydride, diethylaluminum hydride, diisopropylaluminum hydride, dimethylaluminum trimethylsiloxide, dimethylaluminum triethylsiloxide, phenylalane, pentafluorophenylalane, or o-tolylalane.
17. The catalyst system as claimed in claim 5, wherein the at least one metallocene is of the formula III



where

- $M^3$  is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements,
- $R^{10}$  are identical or different and are each a hydrogen atom,  $Si(R^{12})_3$ , or a  $C_1$ - $C_{30}$  group, or two or more radicals  $R^{10}$  may be joined to one another in such a way that the radicals  $R^{10}$  and the atoms of the cyclopentadienyl ring which connect them form a  $C_4$ - $C_{24}$  ring system which may in turn be substituted,
- $R^{11}$  are identical or different and are each a hydrogen atom,  $Si(R^{12})_3$ , or a  $C_1$ - $C_{30}$  group, or two or more radicals  $R^{11}$  may be joined to one another in such a

way that the radicals  $R^{11}$  and the atoms of the cyclopentadienyl ring which connect them form a  $C_4$ - $C_{24}$  ring system which may in turn be substituted,

$R^{12}$  are identical or different and are each a hydrogen atom or a  $C_1$ - $C_{40}$  group,

$l$  is 5 when  $v = 0$ , and  $l$  is 4 when  $v = 1$ ,

$m$  is 5 when  $v = 0$ , and  $m$  is 4 when  $v = 1$ ,

$L^1$  may be identical or different and are each a hydrogen atom, a  $C_1$ - $C_{10}$ -hydrocarbon group, a halogen atom, or  $OR^{16}$ ,  $SR^{16}$ ,  $OSi(R^{16})_3$ ,  $Si(R^{16})_3$ ,  $P(R^{16})_2$  or  $N(R^{16})_2$ , where  $R^{16}$  is a halogen atom, a  $C_1$ - $C_{10}$ -alkyl group, a halogenated  $C_1$ - $C_{10}$ -alkyl group, a  $C_6$ - $C_{20}$ -aryl group or a halogenated  $C_6$ - $C_{20}$ -aryl group, or each  $L^1$  is a toluenesulfonyl, trifluoroacetyl, trifluoroacetoxyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl or 2,2,2-trifluoroethanesulfonyl group,

$o$  is an integer from 1 to 4,

$Z$  is a bridging structural element between the two cyclopentadienyl rings and  $v$  is 0 or 1.

18. A process for preparing a polyolefin which comprises polymerizing one or more olefins in the presence of the catalyst system as claimed in claim 5.

19. The catalyst system as claimed in claim 17,

wherein

$M^3$  is Ti, Zr or Hf,

$R^{10}$  are identical or different and are each a hydrogen atom,  $Si(R^{12})_3$ ,  $C_1$ - $C_{25}$ -alkyl,  $C_2$ - $C_{25}$ -alkenyl,  $C_3$ - $C_{15}$ -alkylalkenyl,  $C_6$ - $C_{24}$ -aryl,  $C_5$ - $C_{24}$ -heteroaryl,  $C_7$ - $C_{30}$ -arylalkyl,  $C_7$ - $C_{30}$ -alkylaryl, fluorinated  $C_1$ - $C_{25}$ -alkyl, fluorinated  $C_6$ - $C_{24}$ -aryl, fluorinated  $C_7$ - $C_{30}$ -arylalkyl, fluorinated  $C_7$ - $C_{30}$ -alkylaryl or  $C_1$ - $C_{12}$ -alkoxy, or two or more radicals  $R^{10}$  may be joined to one another in such a way that the radicals  $R^{10}$  and the atoms of the cyclopentadienyl ring which connect them form a  $C_4$ - $C_{24}$  ring system which may in turn be substituted,

$R^{11}$  are identical or different and are each a hydrogen atom,  $Si(R^{12})_3$ ,  $C_1$ - $C_{25}$ -alkyl,  $C_2$ - $C_{25}$ -alkenyl,  $C_3$ - $C_{15}$ -alkylalkenyl,  $C_6$ - $C_{24}$ -aryl,  $C_5$ - $C_{24}$ -heteroaryl,  $C_5$ - $C_{24}$ -alkylheteroaryl,  $C_7$ - $C_{30}$ -arylalkyl,  $C_7$ - $C_{30}$ -alkylaryl, fluorinated  $C_1$ - $C_{25}$ -alkyl, fluorinated  $C_6$ - $C_{24}$ -aryl, fluorinated  $C_7$ - $C_{30}$ -arylalkyl, fluorinated

C<sub>7</sub>-C<sub>30</sub>-alkylaryl or C<sub>1</sub>-C<sub>12</sub>-alkoxy, or two or more radicals R<sup>11</sup> may be joined to one another in such a way that the radicals R<sup>11</sup> and the atoms of the cyclopentadienyl ring which connect them form a C<sub>4</sub>-C<sub>24</sub> ring system which may in turn be substituted,

- R<sup>12</sup> are identical or different and are each a hydrogen atom, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl, C<sub>1</sub>-C<sub>10</sub>-alkoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>6</sub>-C<sub>10</sub>-fluoroaryl, C<sub>6</sub>-C<sub>10</sub>-aryloxy, C<sub>2</sub>-C<sub>10</sub>-alkenyl, C<sub>7</sub>-C<sub>40</sub>-arylalkyl, C<sub>7</sub>-C<sub>40</sub>-alkylaryl or C<sub>8</sub>-C<sub>40</sub>-arylalkenyl, or
- l is 5 when v = 0, and l is 4 when v = 1,
- m is 5 when v = 0, and m is 4 when v = 1,
- L<sup>1</sup> may be identical or different and are each a hydrogen atom, C<sub>1</sub>-C<sub>10</sub>-alkyl, C<sub>6</sub>-C<sub>10</sub>-aryl, a halogen atom, or OR<sup>16</sup>, SR<sup>16</sup>, OSi(R<sup>16</sup>)<sub>3</sub>, Si(R<sup>16</sup>)<sub>3</sub>, P(R<sup>16</sup>)<sub>2</sub> or N(R<sup>16</sup>)<sub>2</sub>, where R<sup>16</sup> is a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a halogenated C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>6</sub>-C<sub>20</sub>-aryl group or a halogenated C<sub>6</sub>-C<sub>20</sub>-aryl group, or each L<sup>1</sup> is a toluenesulfonyl, trifluoroacetyl, trifluoroacetoxyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl or 2,2,2-trifluoroethanesulfonyl group,
- o is 2,
- Z is a bridging structural element between the two cyclopentadienyl rings and v is 0 or 1..- -

### REMARKS

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. The applicants have corrected an obvious typographical error with respect to the specification. US 5,384,299 was inadvertently typed as US 5,348,299 and this is an obvious typographical error. The applicants have enclosed a copy of both patents. US 5,348,299 relates to an electronic gaming apparatus and not a zwitterionic catalyst.

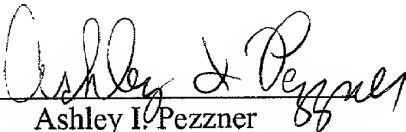
Support for newly added claims 5-12 can be found in the original claim 1. Support for newly added claims 13 and 14 can be found in the specification at page 7. Support for newly added claim 15, can be found in the original claim 2. Support for

newly added claim 16 can be found in the specification at page 49. Support for newly added claims 17 and 19 can be found in the specification at pages 9-11. Support for newly added claim 18 can be found in the original claim 3.

No additional fee is required for the additional claims. If there are any additional fees due in connection with the filing of this response, the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,  
CONNOLLY BOVE LODGE & HUTZ LLP

By   
Ashley I. Pezzner  
Reg. No. 35,646  
Tel. (302) 888-6270

AIP/cam/168394

09080516 011602

APPENDIX I

US-A 5,384,299 [US-A 5,348,299] describes zwitterionic catalyst systems prepared by protolysis from dialkyl-metallocene compounds and salts of the formula  $[R_3NH]^+ [B(C_6F_5)_4]^-$ . C-H Activation as subsequent reaction does not occur here.



Catalyst system

The present invention describes a catalyst system comprising a  
5 metallocene, a cocatalyst, a support material and optionally a  
further organometallic compound. The catalyst system can  
advantageously be used for the polymerization of olefins. Here,  
the use of aluminoxanes such as methylaluminoxane (MAO) as  
cocatalyst is dispensed with and a high catalyst activity and  
10 good polymer morphology are nevertheless achieved.

The role of cationic complexes in Ziegler-Natta polymerization  
using metallocenes is generally recognized (H.H. Brintzinger, D.  
Fischer, R. Mülhaupt, R. Rieger, R. Waymouth, Angew. Chem. 1995,  
15 107, 1255-1283).

MAO has hitherto been the most effective cocatalyst but has the  
disadvantage of having to be used in a large excess, which leads  
to a high undesirable aluminum content in the polymer. The  
20 preparation of cationic alkyl complexes opens the way to MAO-free  
catalysts having a comparable activity, with the cocatalyst being  
able to be used in an almost stoichiometric amount.

The synthesis of "cation-like" metallocene polymerization  
25 catalysts is described in J. Am. Chem. Soc. 1991, 113, 3623. A  
process for preparing salts of the formula  $LMX^+ XA^-$  according to  
the above-described principle is disclosed in EP-A-0 520 732.

EP-A-0 558 158 describes zwitterionic catalyst systems which are  
30 prepared from dialkyl-metallocene compounds and salts of the  
formula  $[R_3NH]^+ [B(C_6H_5)_4]^-$ . The reaction of such a salt with, for  
example,  $Cp_2ZrMe_2$  results in protolysis with elimination of  
methane to form a methyl-zirconocene cation as an intermediate.  
This reacts via C-H-activation to give the zwitterion  
35  $Cp_2Zr^+-(m-C_6H_4)-BPh_3^-$ . In this, the Zr atom is covalently bound to  
a carbon atom of the phenyl ring and is stabilized by agostic  
hydrogen bonds.

US-A-5,348,299 describes zwitterionic catalyst systems prepared  
40 by protolysis from dialkyl-metallocene compounds and salts of the  
formula  $[R_3NH]^+ [B(C_6F_5)_4]^-$ . C-H-Activation as subsequent reaction  
does not occur here.

EP-A-0 426 637 utilizes a process in which the Lewis-acid  $CPh_3^+$   
45 cation is used for abstraction of the methyl group from the metal  
center.  $B(C_6F_5)_4^-$  likewise functions as weakly coordinating anion.

Industrial use of metallocene catalysts requires the catalyst system to be made heterogeneous so as to ensure an appropriate morphology of the resulting polymer. The application of cationic metallocene catalysts based on the abovementioned borate anions to a support is described in WO 91/09882. Here, the catalyst system is formed by application of a dialkyl-metallocene compound and a Brønsted-acid, quaternary ammonium compound having a noncoordinating anion, e.g. tetrakis(pentafluorophenyl)borate, to an inorganic support. The support material is modified beforehand by means of a trialkylaluminum compound.

A disadvantage of this method of application to a support is that only a small part of the metallocene used is immobilized by physisorption on the support material. When the catalyst system is metered into the reactor, the metallocene can easily become detached from the support surface. This leads to a partly homogeneous polymerization which results in an unsatisfactory polymer morphology. WO96/04319 describes a catalyst system in which the cocatalyst is covalently bound to the support material. However, this catalyst system has a low polymerization activity and, in addition, the high sensitivity of the supported cationic metallocene catalysts can lead to problems during introduction into the polymerization system.

It would therefore be desirable to develop a catalyst system which can either be activated before introduction into the reactor or be activated only in the polymerization autoclave.

It is an object of the present invention to provide a catalyst system which avoids the disadvantages of the prior art and nevertheless guarantees high polymerization activities and a good polymer morphology. A further object is to develop a process for preparing this catalyst system which makes it possible for the catalyst system to be activated either before introduction into the polymerization autoclave or only in the polymerization autoclave itself.

We have found that these objects are achieved by a supported catalyst system and a process for preparing it. The present invention further provides for the use of the catalyst system of the present invention in the preparation of polyolefins, and also provides a corresponding polymerization process.

The catalyst system of the present invention comprises

A) at least one metallocene,

B) at least one Lewis base of the formula I



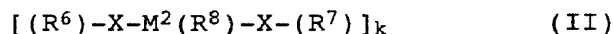
5 where

10  $R^3, R^4, R^5$  are identical or different and are each a hydrogen atom or a  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_6$ - $C_{40}$ -haloaryl,  $C_7$ - $C_{40}$ -alkylaryl or  $C_7$ - $C_{40}$ -arylalkyl group or two or all three of the radicals  $R^3, R^4$  and  $R^5$  may be joined to one another via  $C_2$ - $C_{20}$  units,

15  $M^1$  is an element of main group V of the Periodic Table of the Elements, in particular nitrogen or phosphorus

C) at least one support

20 D) and at least one organoboron or organoaluminum compound which is made up of units of the formula II



where

25  $R^6, R^7$  are identical or different and are each a hydrogen atom, a halogen atom, a boron-free  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl or an  $Si(R^9)_3$  group,

35 where  $R^9$  is a boron-free  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl,

40  $R^8$  can be identical to or different from  $R^6$  and  $R^7$  and is a hydrogen atom, a halogen atom, a  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl or an  $OSi(R^9)_3$  group,

45

X may be identical or different and are each an element of group IV, V or VIa of the Periodic Table of the Elements or an NH group,

5 M<sup>2</sup> is an element of group IIIa of the Periodic Table of the Elements and

k is a natural number from 1 to 100,

10 and is covalently bound to the support.

The compounds of the formula (II) can be in the form of monomers or in the form of linear, cyclic or cage-like oligomers. The index k is the result of Lewis acid-base interactions of the  
15 chemical compound of the formula (II) to form dimers, trimers or higher oligomers.

Particular preference is also given to compounds in which M<sup>2</sup> is aluminum or boron.

20

Preferred compounds of the formula (I) are triethylamine, triisopropylamine, triisobutylamine, tri(n-butyl)amine, N,N-dimethylaniline, N,N-diethylaniline, N,N-2,4,6-pentamethylaniline, dicyclohexylamine, pyridine,  
25 pyrazine, triphenylphosphine, tri(methylphenyl)phosphine, tri(dimethylphenyl)phosphine.

Preferred cocatalytically active chemical compounds of the formula (II) are compounds in which X is an oxygen atom or an NH  
30 group and the radicals R<sup>6</sup> and R<sup>7</sup> are each a boron-free C<sub>1</sub>-C<sub>40</sub>-hydrocarbon radical which may be halogenated, preferably perhalogenated, by halogen such as fluorine, chlorine, bromine or iodine, in particular a halogenated, especially perhalogenated, C<sub>1</sub>-C<sub>30</sub>-alkyl group such as trifluoromethyl, pentachloroethyl,  
35 heptafluoroisopropyl or monofluoroisobutyl or a halogenated C<sub>6</sub>-C<sub>30</sub>-aryl group such as pentafluorophenyl, 2,4,6-trifluorophenyl, heptachloronaphthyl, heptafluoronaphthyl, heptafluorotolyl, 3,5-bis(trifluoromethyl)phenyl, 2,4,6-tris(trifluoromethyl)phenyl, nonafluorobiphenyl or  
40 4-(trifluoromethyl)phenyl. Likewise preferred as R<sup>6</sup> and R<sup>7</sup> are radicals such as phenyl, naphthyl, anisyl, methyl, ethyl, isopropyl, butyl, tolyl, biphenyl or 2,3-dimethylphenyl. Particularly preferred radicals R<sup>6</sup> and R<sup>7</sup> are pentafluorophenyl, phenyl, biphenyl, bisphenylmethylenes,  
45 3,5-bis(trifluoromethyl)phenyl, 4-(trifluoromethyl)phenyl,

nonafluorobiphenyl, bis(pentafluorophenyl)methylene and 4-methylphenyl.

- $R^8$  is particularly preferably a boron-free  $C_1$ - $C_{40}$ -hydrocarbon radical which may be halogenated, preferably perhalogenated, by halogen such as fluorine, chlorine, bromine or iodine, in particular a halogenated, especially perhalogenated,  $C_1$ - $C_{30}$ -alkyl group such as trifluoromethyl, pentachloroethyl, heptafluoroisopropyl or monofluoroisobutyl or a halogenated  $C_6$ - $C_{30}$ -aryl group such as pentafluorophenyl, 2,4,6-trifluorophenyl, heptachloronaphthyl, heptafluoronaphthyl, heptafluorotolyl, 3,5-bis(trifluoromethyl)phenyl, 2,4,6-tris(trifluoromethyl)phenyl, nonafluorobiphenyl or 4-(trifluoromethyl)phenyl. Likewise preferred as  $R^8$  are radicals such as phenyl, naphthyl, anisyl, methyl, ethyl, isopropyl, butyl, tolyl, biphenyl or 2,3-dimethylphenyl. Particularly preferred radicals  $R^8$  are methyl, ethyl, isopropyl, butyl, pentafluorophenyl, phenyl, biphenyl, bisphenylmethylene, 3,5-bis(trifluoromethyl)phenyl, 4-(trifluoromethyl)phenyl, nonafluorobiphenyl, bis(pentafluorophenyl)methylene and 4-methylphenyl.

- Very particularly preferred cocatalytically active chemical compounds of the formula (II) are ones in which X is oxygen, sulfur or an NH group and  $M^2$  is aluminum or boron.

Nonrestrictive examples to illustrate formula II (may also be unfluorinated) are:

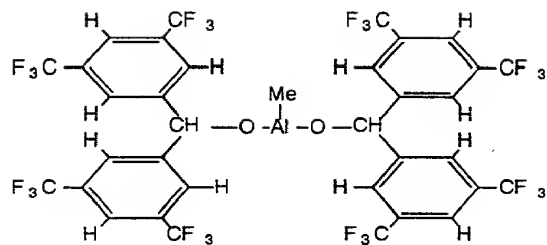
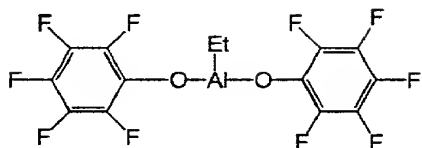
30

35

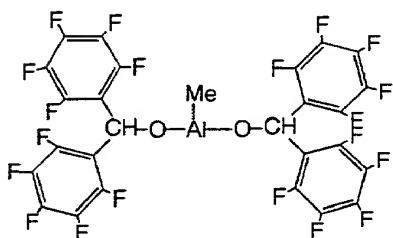
40

45

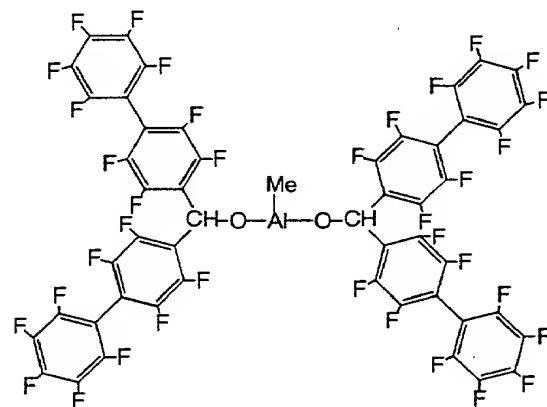
5



10

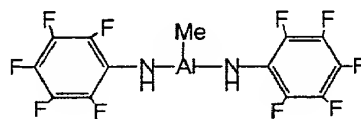
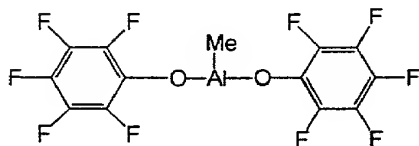


15

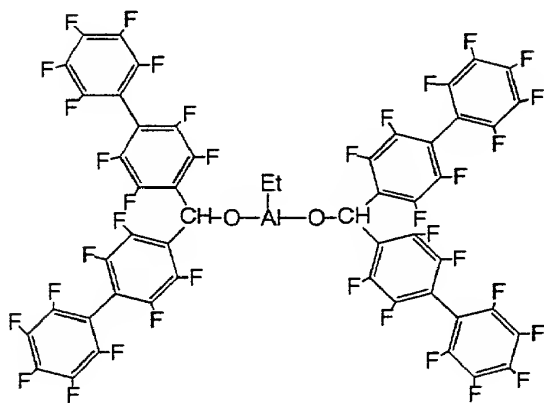


20

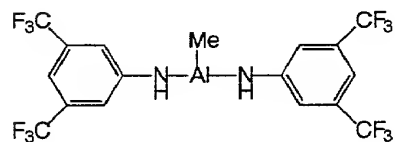
25



30

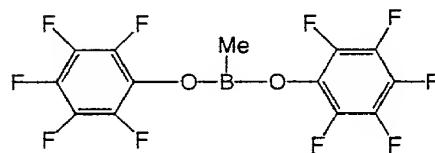
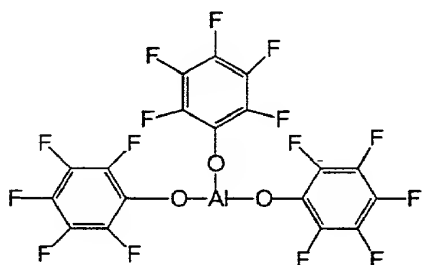


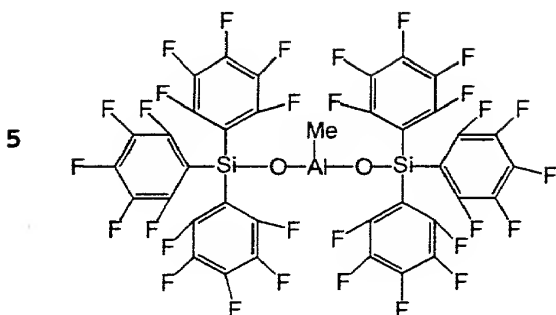
35



40

45





The support component of the catalyst system of the present invention can be any organic or inorganic, inert solid, in particular a porous support such as talc, inorganic oxides and  
15 finely divided polymer powders (e.g. polyolefins).

Suitable inorganic oxides are oxides of elements of groups 2, 3, 4, 5, 13, 14, 15 and 16 of the Periodic Table of the Elements. Examples of oxides preferred as supports include silicon dioxide,  
20 aluminum oxide and also mixed oxides of the two elements and corresponding oxide mixtures. Other inorganic oxides which can be used alone or in combination with the abovementioned preferred oxidic supports are, for example, MgO, ZrO<sub>2</sub>, TiO<sub>2</sub> or B<sub>2</sub>O<sub>3</sub>, to name only a few.

25 The support materials used have a specific surface area in the range from 10 to 1000 m<sup>2</sup>/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of from 1 to 500 μm. Preference is given to supports having a specific surface area in the range  
30 from 50 to 500 μm, a pore volume in the range from 0.5 to 3.5 ml/g and a mean particle size in the range from 5 to 350 μm. Particular preference is given to supports having a specific surface area in the range from 200 to 400 m<sup>2</sup>/g, a pore volume in the range from 0.8 to 3.0 ml/g and a mean particle size of from  
35 10 to 200 μm.

If the support material used naturally has a low moisture content or residual solvent content, dehydration or drying before use can be omitted. If this is not the case, for example when using  
40 silica gel as support material, dehydration or drying is advisable. Thermal dehydration or drying of the support material can be carried out under reduced pressure with simultaneous inert gas blanketing (e.g. nitrogen). The drying temperature is in the range from 100 to 1000°C, preferably from 200 to 800°C. The  
45 parameter pressure is not critical in this case. The duration of the drying process can be from 1 to 24 hours. Shorter or longer drying times are possible provided that equilibrium with the

hydroxyl groups on the support surface can be established under the chosen conditions, which normally takes from 4 to 8 hours.

Dehydration or drying of the support material can also be carried out by chemical means, by reacting the adsorbed water and the hydroxyl groups on the surface with suitable passivating agents. The reaction with the passivating reagent can convert all or some of the hydroxyl groups into a form which leads to no adverse interaction with the catalytically active centers. Suitable passivating agents are, for example, silicon halides and silanes, e.g. silicon tetrachloride, chlorotrimethylsilane, dimethylaminotrichlorosilane, or organometallic compounds of aluminum, boron and magnesium, for example trimethylaluminum, triethylaluminum, triisobutylaluminum, triethylborane, dibutylmagnesium. Chemical dehydration or passivation of the support material is carried out, for example, by reacting a suspension of the support material in a suitable solvent with the passivating reagent in pure form or as a solution in a suitable solvent in the absence of air and moisture. Suitable solvents are, for example, aliphatic or aromatic hydrocarbons such as pentane, hexane, heptane, toluene or xylene. Passivation is carried out at from 25°C to 120°C, preferably from 50°C to 70°C. Higher and lower temperatures are possible. The reaction time is in the range from 30 minutes to 20 hours, preferably from 1 to 5 hours. After chemical dehydration is complete, the support material is isolated by filtration under inert conditions, washed one or more times with suitable inert solvents as have been described above and subsequently dried in a stream of inert gas or under reduced pressure.

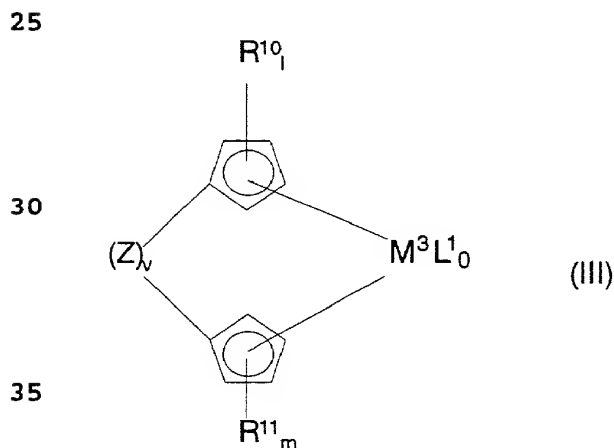
Organic support materials such as finely divided polyolefin powders (e.g. polyethylene, polypropylene or polystyrene) can also be used and should likewise be freed of adhering moisture, solvent residues or other impurities by appropriate purification and drying operations before use.

The chemical compounds of the formula (I) used according to the present invention can be employed together with an organometallic transition metal compound as catalyst system. Organometallic transition metal compounds used can be, for example, metallocene compounds. These may be, for example, bridged or unbridged biscyclopentadienyl complexes as are described, for example, in EP-A-0 129 368, EP-A-0 561 479, EP-A-0 545 304 and EP-A-0 576 970, monocyclopentadienyl complexes such as bridged amidocyclopentadienyl complexes described, for example, in EP-A-0 416 815, multinuclear cyclopentadienyl complexes as described, for example, in EP-A-0 632 063,  $\pi$ -ligand-substituted



tetrahydropentalenes as described, for example, in EP-A-0 659 758 or  $\pi$ -ligand-substituted tetrahydroindenes as described, for example, in EP-A-0 661 300. It is also possible to use organometallic compounds in which the complexing ligand contains no cyclopentadienyl ligand. Examples are diamine complexes of transition groups III and IV of the Periodic Table of the Elements, as are described, for example, in D.H. McConville, et al, *Macromolecules*, 1996, 29, 5241, and D.H. McConville, et al, *J. Am. Chem. Soc.*, 1996, 118, 10008. It is also possible to use diimine complexes of transition group VIII of the Periodic Table of the Elements (e.g.  $\text{Ni}^{2+}$  or  $\text{Pd}^{2+}$  complexes), as are described in Brookhart et al, *J. Am. Chem. Soc.* 1995, 117, 6414, and Brookhart et al, *J. Am. Chem. Soc.*, 1996, 118, 267. 2,6-Bis(imino)pyridyl complexes of transition group VIII of the Periodic Table of the Elements (e.g.  $\text{Co}^{2+}$  or  $\text{Fe}^{2+}$  complexes), as are described in Brookhart et al, *J. Am. Chem. Soc.* 1998, 120, 4049, and Gibson et al, *Chem. Commun.* 1998, 849, can also be used. Furthermore, it is possible to use metallocene compounds whose complexing ligand contains heterocycles. Examples of such compounds are described in WO 98/22486.

Preferred metallocene compounds are unbridged or bridged compounds of the formula (III),



where

40  $\text{M}^3$  is a metal of transition group III, IV, V or VI of the Periodic Table of the Elements, in particular Ti, Zr or Hf,

45  $\text{R}^{10}$  are identical or different and are each a hydrogen atom or  $\text{Si}(\text{R}^{12})_3$ , where  $\text{R}^{12}$  are identical or different and are each a hydrogen atom or a  $\text{C}_1$ - $\text{C}_{40}$  group, preferably  $\text{C}_1$ - $\text{C}_{20}$ -alkyl,  $\text{C}_1$ - $\text{C}_{10}$ -fluoroalkyl,  $\text{C}_1$ - $\text{C}_{10}$ -alkoxy,  $\text{C}_6$ - $\text{C}_{20}$ -aryl,  $\text{C}_6$ - $\text{C}_{10}$ -fluoroaryl,  $\text{C}_6$ - $\text{C}_{10}$ -aryloxy,  $\text{C}_2$ - $\text{C}_{10}$ -alkenyl,

## 10

C<sub>7</sub>-C<sub>40</sub>-arylalkyl, C<sub>7</sub>-C<sub>40</sub>-alkylaryl or C<sub>8</sub>-C<sub>40</sub>-arylalkenyl, or R<sup>10</sup> is a C<sub>1</sub>-C<sub>30</sub> group, preferably C<sub>1</sub>-C<sub>25</sub>-alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C<sub>2</sub>-C<sub>25</sub>-alkenyl, C<sub>3</sub>-C<sub>15</sub>-alkylalkenyl, C<sub>6</sub>-C<sub>24</sub>-aryl, C<sub>5</sub>-C<sub>24</sub>-heteroaryl, C<sub>7</sub>-C<sub>30</sub>-arylalkyl, C<sub>7</sub>-C<sub>30</sub>-alkylaryl, fluorinated C<sub>1</sub>-C<sub>25</sub>-alkyl, fluorinated C<sub>6</sub>-C<sub>24</sub>-aryl, fluorinated C<sub>7</sub>-C<sub>30</sub>-arylalkyl, fluorinated C<sub>7</sub>-C<sub>30</sub>-alkylaryl or C<sub>1</sub>-C<sub>12</sub>-alkoxy, or two or more radicals R<sup>10</sup> may be joined to one another in such a way that the radicals R<sup>10</sup> and the atoms of the cyclopentadienyl ring which connect them form a C<sub>4</sub>-C<sub>24</sub> ring system which may in turn be substituted,

R<sup>11</sup> are identical or different and are each a hydrogen atom or Si(R<sup>12</sup>)<sub>3</sub>, where R<sup>12</sup> are identical or different and are each a hydrogen atom or a C<sub>1</sub>-C<sub>40</sub> group, preferably C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl, C<sub>1</sub>-C<sub>10</sub>-alkoxy, C<sub>6</sub>-C<sub>14</sub>-aryl, C<sub>6</sub>-C<sub>10</sub>-fluoroaryl, C<sub>6</sub>-C<sub>10</sub>-aryloxy, C<sub>2</sub>-C<sub>10</sub>-alkenyl, C<sub>7</sub>-C<sub>40</sub>-arylalkyl, C<sub>7</sub>-C<sub>40</sub>-alkylaryl or C<sub>8</sub>-C<sub>40</sub>-arylalkenyl, or R<sup>11</sup> is a C<sub>1</sub>-C<sub>30</sub> group, preferably C<sub>1</sub>-C<sub>25</sub>-alkyl such as methyl, ethyl, tert-butyl, cyclohexyl or octyl, C<sub>2</sub>-C<sub>25</sub>-alkenyl, C<sub>3</sub>-C<sub>15</sub>-alkylalkenyl, C<sub>6</sub>-C<sub>24</sub>-aryl, C<sub>5</sub>-C<sub>24</sub>-heteroaryl, C<sub>5</sub>-C<sub>24</sub>-alkylheteroaryl, C<sub>7</sub>-C<sub>30</sub>-arylalkyl, C<sub>7</sub>-C<sub>30</sub>-alkylaryl, fluorinated C<sub>1</sub>-C<sub>25</sub>-alkyl, fluorinated C<sub>6</sub>-C<sub>24</sub>-aryl, fluorinated C<sub>7</sub>-C<sub>30</sub>-arylalkyl, fluorinated C<sub>7</sub>-C<sub>30</sub>-alkylaryl or C<sub>1</sub>-C<sub>12</sub>-alkoxy, or two or more radicals R<sup>11</sup> may be joined to one another in such a way that the radicals R<sup>11</sup> and the atoms of the cyclopentadienyl ring which connect them form a C<sub>4</sub>-C<sub>24</sub> ring system which may in turn be substituted,

l is 5 when v = 0, and l is 4 when v = 1,

m is 5 when v = 0, and m is 4 when v = 1,

L<sup>1</sup> may be identical or different and are each a hydrogen atom, a C<sub>1</sub>-C<sub>10</sub>-hydrocarbon group such as C<sub>1</sub>-C<sub>10</sub>-alkyl or C<sub>6</sub>-C<sub>10</sub>-aryl, a halogen atom, or OR<sup>16</sup>, SR<sup>16</sup>, OSi(R<sup>16</sup>)<sub>3</sub>, Si(R<sup>16</sup>)<sub>3</sub>, P(R<sup>16</sup>)<sub>2</sub> or N(R<sup>16</sup>)<sub>2</sub>, where R<sup>16</sup> is a halogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a halogenated C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>6</sub>-C<sub>20</sub>-aryl group or a halogenated C<sub>6</sub>-C<sub>20</sub>-aryl group, or L<sup>1</sup> is a toluenesulfonyl, trifluoroacetyl, trifluoroacetoxyl, trifluoromethanesulfonyl, nonafluorobutanesulfonyl or 2,2,2-trifluoroethanesulfonyl group,

o is an integer from 1 to 4, preferably 2,

## 11

Z is a bridging structural element between the two cyclopentadienyl rings and v is 0 or 1.

Examples of Z are  $M^4R^{13}R^{14}$  groups, where  $M^4$  is carbon, silicon, germanium or tin and  $R^{13}$  and  $R^{14}$  are identical or different and are each a  $C_1$ - $C_{20}$  group such as  $C_1$ - $C_{10}$ -alkyl,  $C_6$ - $C_{14}$ -aryl or trimethylsilyl. Z is preferably  $CH_2$ ,  $CH_2CH_2$ ,  $CH(CH_3)CH_2$ ,  $CH(C_4H_9)C(CH_3)_2$ ,  $C(CH_3)_2$ ,  $(CH_3)_2Si$ ,  $(CH_3)_2Ge$ ,  $(CH_3)_2Sn$ ,  $(C_6H_5)_2Si$ ,  $(C_6H_5)(CH_3)Si$ ,  $(C_6H_5)_2Ge$ ,  $(C_6H_5)_2Sn$ ,  $(CH_2)_4Si$ ,  $CH_2Si(CH_3)_2$ , o- $C_6H_4$  or 2,2'-( $C_6H_4$ )<sub>2</sub>. It is also possible for Z together with one or more radicals  $R^{10}$  and/or  $R^{11}$  to form a monocyclic or polycyclic ring system.

Preference is given to chiral bridged metallocene compounds of the formula (III), in particular those in which v is 1 and one or both cyclopentadienyl rings are substituted so that they form an indenyl ring. The indenyl ring is preferably substituted, in particular in the 2 position, 4 position, 2,4,5 positions, 2,4,6 positions, 2,4,7 positions or 2,4,5,6 positions, by  $C_1$ - $C_{20}$  groups such as  $C_1$ - $C_{10}$ -alkyl or  $C_6$ - $C_{20}$ -aryl, where two or more substituents of the indenyl ring may also together form a ring system.

Chiral bridged metallocene compounds of the formula (III) can be used as pure racemic or pure meso compounds. However, it is also possible to use mixtures of a racemic compound and a meso compound.

Examples of metallocene compounds are:

dimethylsilanediylbis(indenyl)zirconium dichloride

dimethylsilanediylbis(4-naphthyl-indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-benzo-indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(1-naphthyl)-indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(2-naphthyl)-indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride

## 12

dimethylsilanediylbis(2-methyl-4-t-butyl-indenyl)zirconium  
dichloride

dimethylsilanediylbis(2-methyl-4-isopropyl-indenyl)zirconium  
5 dichloride

dimethylsilanediylbis(2-methyl-4-ethyl-indenyl)zirconium  
dichloride

10 dimethylsilanediylbis(2-methyl-4- $\alpha$ -acenaphthindenyl)zirconium  
dichloride

dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride

15 dimethylsilanediylbis(2-ethyl-indenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-ethylindenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium  
20 dichloride

Dimethylsilandiybis(2-methyl-4,5-benzoindenyl)zirconium  
dichloride

25 dimethylsilanediylbis(2-methyl-4,6 diisopropylindenyl)zirconium  
dichloride

dimethylsilanediylbis(2-methyl-4,5 diisopropylindenyl)zirconium  
dichloride

30 dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride

dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride

35 dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-5-isobutylindenyl)zirconium  
dichloride

40 dimethylsilanediylbis(2-methyl-5-t-butylindenyl)zirconium  
dichloride

methyl(phenyl)silanediylbis(2-methyl-4-phenylindenyl)zirconium  
dichloride

45

## 13

methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)  
zirconium dichloride

methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)zirconium  
5 dichloride

methyl(phenyl)silanediylbis(2-methyl-4,5-benzoindenyl)zirconium  
dichloride

10 methyl(phenyl)silanediylbis(2-methyl-4,5-(methylbenzo)indenyl)  
zirconium dichloride

methyl(phenyl)silanediylbis(2-methyl-4,5-(tetramethylbenzo)-  
indenyl)zirconium dichloride

15

methyl(phenyl)silanediylbis(2-methyl-4- $\alpha$ -acenaphthindenyl)-  
zirconium dichloride

methyl(phenyl)silanediylbis(2-methylindenyl)zirconium dichloride

20

methyl(phenyl)silanediylbis(2-methyl-5-isobutylindenyl)zirconium  
dichloride

1,2-ethanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride

25

1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride

1,2-ethanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium  
dichloride

30

1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium  
dichloride

1,4-butanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride

35

1,2-ethanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride

1,2-ethanediylbis(2,4,7-trimethylindenyl)zirconium dichloride

40 1,2-ethanediylbis(2-methyl-indenyl)zirconium dichloride

1,4-butanediylbis(2-methylindenyl)zirconium dichloride

[4-( $\eta^5$ -cyclopentadienyl)-4,6,6-trimethyl-( $\eta^5$ -4,5-tetrahydro-  
45 pentalene)]dichlorozirconium

## 14

[4-( $\eta^5$ -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl-( $\eta^5$ -4,5-tetrahydropentalene)]dichlorozirconium

5 [4-( $\eta^5$ -3'-isopropylcyclopentadienyl)-4,6,6-trimethyl-( $\eta^5$ -4,5-tetrahydropentalene)]dichlorozirconium

[4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorotitanium

10 [4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorozirconium

[4-( $\eta^5$ -cyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorohafnium

15

[4-( $\eta^5$ -3'-tert-butylcyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorotitanium

20 4-( $\eta^5$ -3'-isopropylcyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorotitanium

4-( $\eta^5$ -3'-methylcyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorotitanium

25 4-( $\eta^5$ -3'-trimethylsilylcyclopentadienyl)-2-trimethylsilyl-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorotitanium

4-( $\eta^5$ -3'-tert-butylcyclopentadienyl)-4,7,7-trimethyl-( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichlorozirconium

30

(tertbutylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilyldichlorotitanium

35 (tertbutylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyl-dichlorotitanium-dichlorotitanium

(methylanido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilyldichlorotitanium

40 (methylanido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyl-dichlorotitanium

(tert-butylamido)(2,4-dimethyl-2,4-pentadien-1-yl)dimethylsilyldichlorotitanium

45

bis(cyclopentadienyl)zirconium dichloride

bis(n-butylcyclopentadienyl)zirconium dichloride

bis(1,3-dimethylcyclopentadienyl)zirconium dichloride

- 5 tetrachloro[1-[bis( $\eta^5$ -1H-inden-1-ylidene)methylsilyl]-3- $\eta^5$ -cyclopenta-2,4-dien-1-ylidene)-3- $\eta^5$ -9H-fluoren-9-ylidene)butane]dizirconium

- 10 tetrachloro[2-[bis( $\eta^5$ -2-methyl-1H-inden-1-ylidene)methoxysilyl]-5-( $\eta^5$ -2,3,4,5-tetramethylcyclopenta-2,4-dien-1-ylidene)-5-( $\eta^5$ -9H-fluoren-9-ylidene)hexane]dizirconium

- tetrachloro[1-[bis( $\eta^5$ -1H-inden-1-ylidene)methylsilyl]-6-( $\eta^5$ -cyclopenta-2,4-dien-1-ylidene)-6-( $\eta^5$ -9H-fluoren-9-ylidene)-3-oxa-  
15 heptane]dizirconium

dimethylsilanediylbis(2-methyl-4-(tert-butylphenylindenyl)-zirconium dichloride

- 20 dimethylsilanediylbis(2-methyl-4-(4-methylphenylindenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(4-ethylphenylindenyl)zirconium dichloride

- 25 dimethylsilanediylbis(2-methyl-4-(4-trifluoromethylphenylindenyl)zirconium dichloride

- dimethylsilanediylbis(2-methyl-4-(4-methoxyphenylindenyl)-  
30 zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4-tert-butylphenylindenyl)-zirconium dichloride

- 35 dimethylsilanediylbis(2-ethyl-4-(4-methylphenylindenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4-ethylphenylindenyl)zirconium dichloride

- 40 dimethylsilanediylbis(2-ethyl-4-(4-trifluoromethylphenylindenyl)zirconium dichloride

- dimethylsilanediylbis(2-ethyl-4-(4-methoxyphenylindenyl)zirconium  
45 dichloride

dimethylsilanediylbis(2-methyl-4-(4-tert-butylphenyl)indenyl)  
zirconium dimethyl

```
dimethylsilanediylbis(2-methyl-4-(4-methylphenylindenyl)zirconium
5 dimethyl
```

dimethylsilanediylbis(2-methyl-4-(4-ethylphenylindenyl)zirconium  
dimethyl

10 dimethylsilanediylbis(2-methyl-4-(4-trifluoromethylphenylindenyl)  
zirconium dimethyl

dimethylsilanediylbis(2-methyl-4-(4-methoxyphenylindenyl)zirconium dimethyl

15 dimethylsilanediylbis(2-ethyl-4-(4-tert-butylphenylindenyl)zirconium dimethyl

dimethylsilanediylbis(2-ethyl-4-(4-methylphenylindenyl)zirconium  
20 dimethyl

dimethylsilanediylbis(2-ethyl-4-(4-ethylphenylindenyl)zirconium  
diethyl

25 dimethylsilanediylbis(2-ethyl-4-(4-trifluoromethylphenylindenyl)  
zirconium dimethyl

dimethylsilanediylbis(2-ethyl-4-(4-methoxyphenylindenyl)zirconium  
dimethyl

30 dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
35 hafnuim dichloride

dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)titanium dichloride

40 dimethylsilanediylbis(2-methyl-4-(4'-methylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(4'-n-propylphenyl)indenyl)  
zirconium dichloride

45



17

dimethylsilanediylbis(2-methyl-4-(4'-n-butylphenyl)indenyl)zirconium dichloride

5 dimethylsilanediylbis(2-methyl-4-(4'-hexylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-(4'-sec-butylphenyl)indenyl)zirconium dichloride

10 dimethylsilanediylbis(2-ethyl-4-phenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4'-methylphenyl)indenyl)zirconium dichloride

15 dimethylsilanediylbis(2-ethyl-4-(4'-ethylphenyl)indenyl)zirconium dichloride

20 dimethylsilanediylbis(2-ethyl-4-(4'-n-propylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4'-n-butylphenyl)indenyl)zirconium dichloride

25 dimethylsilanediylbis(2-ethyl-4-(4'-hexylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4'-pentylphenyl)indenyl)zirconium dichloride

30 dimethylsilanediylbis(2-ethyl-4-(4'-cyclohexylphenyl)indenyl)zirconium dichloride

35 dimethylsilanediylbis(2-ethyl-4-(4'-sec-butylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dichloride

40 dimethylsilanediylbis(2-n-propyl-4-phenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-n-propyl-4-(4'-methylphenyl)indenyl)zirconium dichloride

45

## 18

dimethylsilanediylbis(2-n-propyl-4-(4'-ethylphenyl)-indenyl)  
zirconium dichloride

dimethylsilanediylbis(2-n-propyl-4-(4'-isopropylphenyl)indenyl)  
5 zirconium dichloride

dimethylsilanediylbis(2-n-propyl-4-(4'-n-butylphenyl)indenyl)zir-  
conium dichloride

10 dimethylsilanediylbis(2-n-propyl-4-(4'-hexylphenyl)indenyl)zirco-  
nium dichloride

dimethylsilanediylbis(2-n-propyl-4-(4'-cyclohexylphenyl)indenyl)  
zirconium dichloride

15 dimethylsilanediylbis(2-n-propyl-4-(4'-sec-butylphenyl)indenyl)  
zirconium dichloride

dimethylsilanediylbis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)  
20 zirconium dichloride

dimethylsilanediylbis(2-n-butyl-4-phenyl)indenyl)zirconium  
dichloride

25 dimethylsilanediylbis(2-n-butyl-4-(4'-methylphenyl)indenyl)zirco-  
nium dichloride

dimethylsilanediylbis(2-n-butyl-4-(4'-ethylphenyl)indenyl)zirco-  
nium dichloride

30 dimethylsilanediylbis(2-n-butyl-4-(4'-n-propylphenyl)indenyl)zir-  
conium dichloride

dimethylsilanediylbis(2-n-butyl-4-(4'-isopropylphenyl)indenyl)  
35 zirconium dichloride

dimethylsilanediylbis(2-n-butyl-4-(4'-n-butylphenyl)indenyl)  
zirconium dichloride

40 dimethylsilanediylbis(2-n-butyl-4-(4'-hexylphenyl)indenyl)zirco-  
nium dichloride

dimethylsilanediylbis(2-n-butyl-4-(4'-cyclohexylphenyl)indenyl)  
zirconium dichloride

45

dimethylsilanediybis(2-n-butyl-4-(4'-sec-butylphenyl)indenyl)  
zirconium dichloride

dimethylsilanediylbis(2-n-butyl-4-(4'-tert-butylphenyl)indenyl)

5 zirconium dichloride

dimethylsilanediylbis(2-hexyl-4-phenyl)indenyl)zirconium  
dichloride

10 dimethylsilanediylbis(2-hexyl-4-(4'-methylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-hexyl-4-(4'-ethylphenyl)indenyl)zirconium  
dichloride

15

dimethylsilanediylbis(2-hexyl-4-(4'-n-propylphenyl)indenyl)zirconium dichloride

dimethylsilanediylbis(2-hexyl-4-(4'-isopropylphenyl)indenyl)

20 zirconium dichloride

dimethylsilanediylbis(2-hexyl-4-(4'-n-butylphenyl)indenyl)zirconium dichloride

25 dimethylsilanediylbis(2-hexyl-4-(4'-hexylphenyl)indenyl)zirconium  
dichloride

dimethylsilanediylbis(2-hexyl-4-(4'-cyclohexylphenyl)indenyl)zirconium dichloride

**30**

dimethylsilanediyldibis(2-hexyl-4-(4'-sec-butylphenyl)indenyl)  
zirconium dichloride

dimethylsilanediylbis(2-hexyl-4-(4'-tert-butylphenyl)indenyl)zir-

35 conium dichloride

dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium bis(dimethylamide)

40 dimethylsilanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium dibenzyl

dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium dimethyl

45

- dimethylgermanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium dichloride
- dimethylgermanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)  
5 hafnium dichloride
- dimethylgermanediylbis(2-propyl-4-(4'-tert-butylphenyl)indenyl)  
titanium dichloride
- 10 dimethylgermanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium dichloride
- ethylidenebis(2-ethyl-4-phenyl)indenyl)zirconium dichloride
- 15 ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
dichloride
- ethylidenebis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
dichloride
- 20 ethylidenebis(2-n-butyl-4-(4'-tert-butylphenyl)indenyl)titanium  
dichloride
- ethylidenebis(2-hexyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
25 dibenzyl
- ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)hafnium  
dibenzyl
- 30 ethylidenebis(2-methyl-4-(4'-tert-butylphenyl)indenyl)titanium  
dibenzyl
- ethylidenebis(2-methyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
dichloride
- 35 ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)hafnium  
dimethyl
- ethylidenebis(2-n-propyl-4-phenyl)indenyl)titanium dimethyl
- 40 ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
bis(dimethylamide)
- ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)hafnium  
45 bis(dimethylamide)

## 21

ethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)titanium  
bis(dimethylamide)

methylethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
5 nium dichloride

methylethylidenebis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)hafnium  
dichloride

10 phenylphosphinediyl(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
dichloride

phenylphosphinediyl(2-methyl-4-(4'-tert-butylphenyl)indenyl)  
zirconium dichloride

15 phenylphosphinediyl(2-ethyl-4-(4'-tert-butylphenyl)indenyl)zirconium  
dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-methyl  
20 phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-methyl  
phenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-methyl  
phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-  
methylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-  
methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-  
35 methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-  
methylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-  
methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-  
4-(4'-methylphenylindenyl)zirconium dichloride

45

## 22

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-methylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

45

## 23

dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)-(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride

45

## 24

- dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-ethylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 45



## 25

- dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-n-propylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)-(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride
- 45

## 26

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-  
(2-methyl-4-(4'-isopropylphenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-  
isopropylphenylindenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-  
isopropylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-iso-  
propylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-  
isopropylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-  
isopropylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-n-  
butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-n-  
butylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-n-  
butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-  
(4'-n-butylphenylindenyl)zirconium dichloride

45

dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)-(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

15

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

30

dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride

45

## 28

- dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-n-butylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride
- 45

## 29

dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

15

dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-s-butylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

30

dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)-(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

45

## 30

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-  
(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-tert-  
5 butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-tert-  
butylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-tert-  
butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-  
tert-butylphenylindenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-  
tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-tert-  
20 butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-tert-  
butylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-tert-  
butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-  
tert-butylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-  
tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-n-pen-  
35 tylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-n-pen-  
tylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-n-pen-  
tylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-  
(4'-n-pentylphenylindenyl)zirconium dichloride

45

## 31

- dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 45

- dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-n-pentylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 45



- dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-n-hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- 45

- dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-  
(2-methyl-4-(4'-cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-  
5 cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-cyclo-  
20 hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-cyclo  
hexylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-cyclo  
hexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-  
cyclohexylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-tri-  
35 methylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-tri-  
methylsilylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-tri-  
methylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-  
(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 45

- dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)-(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)-(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride
- 45

## 36

dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-trimethylsilylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

15 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

35 dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride

45

- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- 10 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-adamantylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 25 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 40 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 45

- dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 5 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 10 (trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 15 dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 20 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 25 (trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 30 dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- 35 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-tris(trifluoromethyl)methylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-4-azapentalene)(2-ethyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride
- 40 butylphenylindenyl)zirconium dichloride
- dimethylsilanediyl(2-methyl-5,6-di-hydro-4-azapentalene)(2-ethyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride
- 45 dimethylsilanediyl(2-methyl-4-azapentalene)(2-ethyl-4-(4'-tert-butylphenyl-tetrahydroindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-5-azapentalene)(2-n-butyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

Ethyliden(2-methyl-6-azapentalene)(2-methyl-4-(4'-tert-butyl-  
5 phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-trimethylsilyl-4-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-N-tolyl-5-azapentalene)(2-n-propyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

Dimethylgermyldiyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

15 Methyleneethyliden(2,5-dimethyl-4-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

20 dimethylsilanediyl(2,5-di-iso-propyl-6-azapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2,6-dimethyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

25 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(6'-tert-butyl-naphthylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4-(6'-tert-butylanthracenylindenyl)zirconium dichloride

30 dimethylsilanediyl(2-methyl-4-phosphapentalen)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

diphenylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

35 methylphenylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

40 methylenidene(2,5-dimethyl-4-thiapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylmethylenidene(2,5-dimethyl-6-thiapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

diphenylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

diphenylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-(4'-tert-butylphenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methylindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-azapentalene)(2-methylindenyl)zirconium dichloride

15

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methylindenyl)zirconium dichloride

25 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methylindenyl)zirconium dichloride

30

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methylindenyl)zirconium dichloride

35

dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methylindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methylindenyl)zirconium dichloride

45



## 41

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methylindenyl)  
zirconium dichloride

5 dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methylindenyl)  
zirconium dichloride

dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methylindenyl)  
zirconium dichloride

10 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methylindenyl)  
zirconium dichloride

dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methylindenyl)  
zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methylindenyl)  
zirconium dichloride

20 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methylindenyl)  
zirconium dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(indenyl)zirconium  
dichloride

25 dimethylsilanediyl(2-methyl-5-azapentalene)(indenyl)zirconium  
dichloride

dimethylsilanediyl(2-methyl-6-azapentalene)(indenyl)zirconium  
dichloride

30 dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(indenyl)zir-  
conium dichloride

35 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(indenyl)zir-  
conium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(indenyl)zir-  
conium dichloride

40 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(indenyl)zirconium  
dichloride

dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(indenyl)zirconium  
dichloride

45

## 42

dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(indenyl)  
zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(indenyl)  
5 zirconium dichloride

dimethylsilanediyl(2-methyl-4-thiapentalene)(indenyl)zirconium  
dichloride

10 dimethylsilanediyl(2-methyl-5-thiapentalene)(indenyl)zirconium  
dichloride

dimethylsilanediyl(2-methyl-6-thiapentalene)(indenyl)zirconium  
dichloride

15 dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(indenyl)zirco-  
nium dichloride

dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(indenyl)zirco-  
20 nium dichloride

dimethylsilanediyl(2-methyl-4-oxapentalene)(indenyl)zirconium  
dichloride

25 dimethylsilanediyl(2-methyl-5-oxapentalene)(indenyl)zirconium  
dichloride

dimethylsilanediyl(2-methyl-6-oxapentalene)(indenyl)zirconium  
dichloride

30 dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(indenyl)zirconium  
dichloride

dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(indenyl)zirconium  
35 dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

45

dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

10 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4-phenyl  
indenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4-phenyl  
indenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl  
20 -4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

25 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4-  
35 phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4-phenyl-indenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4-phenyl-  
indenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

5 dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4-phenylindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-5-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

15 dimethylsilanediyl(2-methyl-N-phenyl-4-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

20 dimethylsilanediyl(2-methyl-N-phenyl-5-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-N-phenyl-6-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

25 dimethylsilanediyl(2,5-dimethyl-4-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

30 dimethylsilanediyl(2,5-dimethyl-N-phenyl-4-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

35 dimethylsilanediyl(2,5-dimethyl-N-phenyl-6-azapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-thiapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

40 dimethylsilanediyl(2-methyl-5-thiapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-thiapentalene)(2-methyl-4,5-benzindenyl)zirconium dichloride

## 45

dimethylsilanediyl(2,5-dimethyl-4-thiapentalene)(2-methyl-4,5-benzoindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-thiapentalene)(2-methyl-4,5-  
5 benzoindenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-4-oxapentalene)(2-methyl-4,5-benzo-  
indenyl)zirconium dichloride

10 dimethylsilanediyl(2-methyl-5-oxapentalene)(2-methyl-4,5-benzo-  
indenyl)zirconium dichloride

dimethylsilanediyl(2-methyl-6-oxapentalene)(2-methyl-4,5-benzo-  
indenyl)zirconium dichloride

15 dimethylsilanediyl(2,5-dimethyl-4-oxapentalene)(2-methyl-4,5-ben-  
zoindenyl)zirconium dichloride

dimethylsilanediyl(2,5-dimethyl-6-oxapentalene)(2-methyl-4,5-ben-  
20 zoindenyl)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-azapentalene)zirconium  
dichloride

25 dimethylsilanediylbis(2-methyl-5-azapentalene)zirconium  
dichloride

dimethylsilanediylbis(2-methyl-6-azapentalene)zirconium  
dichloride

30 dimethylsilanediylbis(2-methyl-N-phenyl-4-azapentalene)zirconium  
dichloride

dimethylsilanediylbis(2-methyl-N-phenyl-5-azapentalene)zirconium  
35 dichloride

dimethylsilanediylbis(2-methyl-N-phenyl-6-azapentalene)zirconium  
dichloride

40 dimethylsilanediylbis(2,5-dimethyl-4-azapentalene)zirconium  
dichloride

dimethylsilanediylbis(2,5-dimethyl-6-azapentalene)zirconium  
dichloride

45

0560926 04603

## 46

dimethylsilanediylbis(2,5-dimethyl-N-phenyl-4-azapentalene)zirconium dichloride

dimethylsilanediylbis(2,5-dimethyl-N-phenyl-6-azapentalene)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-thiapentalene)zirconium dichloride

10 dimethylsilanediylbis(2-methyl-5-thiapentalene)zirconium dichloride

dimethylsilanediylbis(2-methyl-6-thiapentalene)zirconium dichloride

15 dimethylsilanediylbis(2,5-dimethyl-4-thiapentalene)zirconium dichloride

dimethylsilanediylbis(2,5-dimethyl-6-thiapentalene)zirconium dichloride

dimethylsilanediylbis(2-methyl-4-oxapentalene)zirconium dichloride

25 dimethylsilanediylbis(2-methyl-5-oxapentalene)zirconium dichloride

dimethylsilanediylbis(2-methyl-6-oxapentalene)zirconium dichloride

30 dimethylsilanediylbis(2,5-dimethyl-4-oxapentalene)zirconium dichloride

dimethylsilanediylbis(2,5-dimethyl-6-oxapentalene)zirconium dichloride

Further examples of metallocenes which can be used for the purposes of the present invention are metallocenes as listed above in which the zirconium fragment "zirconium dichloride" is replaced by

zirconium monochloride mono(2,4-di-tert-butylphenoxide)

zirconium monochloride mono(2,6-di-tert-butylphenoxide)

zirconium monochloride mono(3,5-di-tert-butylphenoxide)

- zirconium monochloride mono(2,6-di-sec-butylphenoxide)
- zirconium monochloride mono(2,4-di-methylphenoxide)
- 5 zirconium monochloride mono(2,3-di-methylphenoxide)
- zirconium monochloride mono(2,5-di-methylphenoxide)
- zirconium monochloride mono(2,6-di-methylphenoxide)
- 10 zirconium monochloride mono(3,4-di-methylphenoxide)
- zirconium monochloride mono(3,5-di-methylphenoxide)
- 15 zirconium monochloride monophenoxide
- zirconium monochloride mono(2-methylphenoxide)
- zirconium monochloride mono(3-methylphenoxide)
- 20 zirconium monochloride mono(4-methylphenoxide)
- zirconium monochloride mono(2-ethylphenoxide)
- 25 zirconium monochloride mono(3-ethylphenoxide)
- zirconium monochloride mono(4-ethylphenoxide)
- zirconium monochloride mono(2-sec-butylphenoxide)
- 30 zirconium monochloride mono(2-tert-butylphenoxide)
- zirconium monochloride mono(3-tert-butylphenoxide)
- 35 zirconium monochloride mono(4-sec-butylphenoxide)
- zirconium monochloride mono(4-tert-butylphenoxide)
- zirconium monochloride mono(2-isopropyl-5-methylphenoxide)
- 40 zirconium monochloride mono(4-isopropyl-3-methylphenoxide)
- zirconium monochloride mono(5-isopropyl-2-methylphenoxide)
- 45 zirconium monochloride mono(5-isopropyl-3-methylphenoxide)

05930926-0460

## 48

zirconium monochloride mono(2,4-bis-(2-methyl-2-butyl)-phenoxide)

zirconium monochloride mono(2,6-di-tert-butyl-4-methyl-phenoxide)

5 zirconium monochloride mono(4-nonylphenoxide)

zirconium monochloride mono(1-naphthoxide)

zirconium monochloride mono(2-naphthoxide)

10

zirconium monochloride mono(2-phenylphenoxide)

zirconium monochloride mono(tert-butoxid)

15 zirconium monochloride mono(N-methylanilide)

zirconium monochloride mono(2-tert-butylanilide)

zirconium monochloride mono(tert-butylamide)

20

zirconium monochloride mono(diisopropylamide)

zirconium monochloride monomethyl

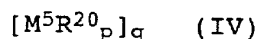
25 zirconium monochloride monobenzyl

zirconium monochloride mononeopentyl.

Preference is also given to the corresponding dimethylzirconium

30 compounds, the corresponding  $\eta^4$ -butadienezirconium compounds and the corresponding compounds having a 1,2-(1-methylethanediy), 1,2-(1,1-dimethylethanediy) or 1,2-(1,2-dimethylethanediy) bridge.

35 The catalyst system of the present invention can further comprise an organometallic compound of the formula (IV)



40 where

$M^5$  is an element of main group I, II or III of the Periodic Table of the Elements, preferably lithium, magnesium or aluminum, in particular aluminum,

45



R<sup>20</sup> are identical or different and are each a hydrogen atom, a halogen atom or a C<sub>1</sub>-C<sub>40</sub> group such as C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>6</sub>-C<sub>40</sub>-aryl, C<sub>7</sub>-C<sub>40</sub>-arylalkyl or C<sub>7</sub>-C<sub>40</sub>-alkylaryl,

5 p is an integer from 1 to 3 and

q is an integer from 1 to 4.

The organometallic compounds of the formula (IV) are likewise  
10 unchanged Lewis acids.

Examples of preferred organometallic compounds of the formula (IV) are trimethylaluminum, triethylaluminum, triisopropylaluminum, trihexylaluminum, trioctylaluminum,  
15 tri-n-butylaluminum, tri-n-propylaluminum, triisoprenylaluminum, dimethylaluminum monochloride, diethylaluminum monochloride, diisobutylaluminum monochloride, methylaluminum sesquichloride, ethylaluminum sesquichloride, dimethylaluminum hydride, diethylaluminum hydride, diisopropylaluminum hydride,  
20 dimethylaluminum trimethylsiloxide, dimethylaluminum triethylsiloxide, phenylalane, pentafluorophenylalane, o-tolylalane.

The catalyst system of the present invention is obtainable by  
25 reacting a Lewis base of the formula (I) and an organoboron or organoaluminum compound made up of units of the formula (II) with a support. This is followed by reaction with a solution or suspension of one or more metallocene compounds of the formula (III) and optionally one or more organometallic compounds of the  
30 formula (IV).

The activation of the catalyst system can thereby be carried out either before its introduction into the reactor or else only in the reactor itself. The present invention also describes a  
35 process for preparing polyolefins. The addition of a further chemical compound as additive prior to the polymerization can be of additional advantage.

To prepare the catalyst system of the present invention, the  
40 support material is suspended in an organic solvent. Suitable solvents are aromatic or aliphatic solvents such as hexane, heptane, toluene or xylene or halogenated hydrocarbons such as methylene chloride or halogenated aromatic hydrocarbons such as o-dichlorobenzene. The support can be pretreated beforehand with  
45 a compound of the formula (IV). Subsequently, one or more compounds of the formula (I) is/are added to this suspension, with the reaction time being able to be from 1 minute to 48

hours, preferably from 10 minutes to 2 hours. The product can be isolated from the reaction solution and subsequently resuspended, or else the reaction solution can be reacted directly with a cocatalytically active organoboron or organoaluminum compound of the formula (II). The reaction time here is from 1 minute to 48 hours, preferably from 10 minutes to 2 hours. To prepare the catalyst system of the present invention, one or more Lewis bases of the formula (I) can be reacted with one or more cocatalytically active organoboron or organoaluminum compounds of the formula (II). Preference is given to reacting from 1 to 4 equivalents of a Lewis base of the formula (I) with one equivalent of a cocatalytically active compound. Particular preference is given to reacting one equivalent of a Lewis base of the formula (I) with one equivalent of a cocatalytically active compound. The reaction product of this reaction is a metallocenium-forming compound which fixed covalently to the support material. It will hereinafter be referred to as modified support material. The reaction mixture is subsequently filtered and the solid washed with one of the abovementioned solvents. The modified support material is then dried in a high vacuum. However, the addition of the individual components can also be carried out in any other order.

The application of one or more metallocene compounds, preferably of the formula (III), and one or more organometallic compounds of the formula (IV) to the modified support material is preferably carried out by dissolving or suspending one or more metallocene compounds of the formula (III) in one of the above-described solvents and subsequently reacting it with one or more compounds of the formula (IV), which is/are preferably likewise in dissolved or suspended form. The stoichiometric ratio of metallocene compound of the formula (III) to organometallic compound of the formula (IV) is from 100 : 1 to  $10^{-4}$  : 1. The ratio is preferably from 1 : 1 to  $10^{-2}$  : 1. The modified support material can be placed together with one of the abovementioned solvents either directly in the polymerization reactor or in a reaction flask. This is followed by the addition of the mixture of a metallocene compound of the formula (III) and an organometallic compound of the formula (IV). However, it is also possible for one or more metallocene compounds of the formula (III) to be added to the modified support material without prior addition of an organometallic compound of the formula (IV).

The ratio of modified support to metallocene compound of the formula (III) is preferably from 10g : 1  $\mu$ mol to  $10^{-2}$ g : 1  $\mu$ mol. The stoichiometric ratio of metallocene compound of the formula (III) to the cocatalytically active chemical compound of the

formula (II) is from 100 : 1 to  $10^{-4}$  : 1, preferably from 1 : 1 to  $10^{-2}$  : 1.

The supported catalyst system can be used directly for  
5 polymerization. However, it is also possible for the solvent to be removed and the solid then to be used in resuspended form for the polymerization. The advantage of this activation method is that it offers the option of allowing the polymerization-active catalyst system to be formed only in the reactor. This prevents  
10 partial decomposition of the air-sensitive catalyst from occurring during its introduction into the reactor.

The present invention also describes a process for preparing an olefin polymer in the presence of the catalyst system of the  
15 present invention. The polymerization can be either a homopolymerization or a copolymerisation.

Preference is given to polymerizing olefins of the formula  $R-CH=CH-R^{\beta}$ , where R and  $R^{\beta}$  are identical or different and are each  
20 a hydrogen atom, a halogen atom, an alkoxy, hydroxy, hydroxyalkyl, aldehyde, carboxylic acid or carboxylic ester group or a saturated or unsaturated hydrocarbon radical having from 1 to 20 carbon atoms, in particular from 1 to 10 carbon atoms, which may be substituted by an alkoxy, hydroxy, hydroxyalkyl,  
25 aldehyde, carboxylic acid or carboxylic ester group, or  $R^{\alpha}$  and  $R^{\beta}$  together with the atoms connecting them form one or more rings. Examples of such olefins are 1-olefins such as ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, styrene, cyclic olefins such as norbornene, vinylnorbornene,  
30 tetracyclododecene, ethylenenorbornene, dienes such as 1,3-butadiene or 1,4-hexadiene, biscyclopentadiene or methyl methacrylate.

Particular preference is given to homopolymerizing propylene or  
35 ethylene, copolymerizing ethylene with one or more  $C_3$ - $C_{20}$ -1-olefins, in particular propylene, and/or one or more  $C_4$ - $C_{20}$ -dienes, in particular 1,3-butadiene, or copolymerizing norbornene and ethylene.

40 The polymerization is preferably carried out at from  $-60$  to  $300^{\circ}\text{C}$ , particularly preferably from  $30$  to  $250^{\circ}\text{C}$ . The pressure is from 0.5 to 2500 bar, preferably from 2 to 1500 bar. The polymerization can be carried out continuously or batchwise, in one or more stages, in solution, in suspension, in the gas phase or in a  
45 supercritical medium.

## 52

The supported catalyst system can either be formed directly in the polymerization system or it can be isolated as a dry powder or as a powder still moist with solvent and then resuspended and metered as a suspension in an inert suspension medium into the  
5 polymerization system.

A prepolymerization can be carried out with the aid of the catalyst system of the present invention. The prepolymerization is preferably carried out using the (or one of the) olefin(s)  
10 used in the polymerization.

To prepare olefin polymers having a broad molecular weight distribution, preference is given to using catalyst systems comprising two or more different transition metal compounds, e.g.  
15 metallocenes.

To remove catalyst poisons present in the olefin, purification using an aluminum alkyl, for example trimethylaluminum, triethylaluminum or triisobutylaluminum, is advantageous. This  
20 purification can be carried out either in the polymerization system itself or the olefin is brought into contact with the Al compound and subsequently separated off again prior to introduction into the polymerization system.

25 As molar mass regulator and/or to increase the activity, hydrogen is added if necessary. The total pressure in the polymerization system is from 0.5 to 2500 bar, preferably from 2 to 1500 bar.

The catalyst system of the present invention is employed in a  
30 concentration, based on the transition metal, of preferably from  $10^{-3}$  to  $10^{-8}$  mol, more preferably from  $10^{-4}$  to  $10^{-7}$  mol, of transition metal per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume.

Suitable solvents for preparing both the supported chemical  
35 compound according to the present invention and also the catalyst system of the present invention are aliphatic or aromatic solvents such as hexane or toluene, ether solvents such as tetrahydrofuran or diethyl ether or halogenated hydrocarbons such as methylene chloride or halogenated aromatic hydrocarbons such  
40 as o-dichlorobenzene.

Before introduction of the catalyst system of the present invention or before activation of the catalyst system of the present invention in the polymerization system, an alkylaluminum  
45 compound such as trimethylaluminum, triethylaluminum, triisobutylaluminum, trioctylaluminum or isoprenylaluminum can additionally be introduced into the reactor to make the

- polymerization system inert (for example to remove catalyst poisons present in the olefin). This is added to the polymerization system in a concentration of from 200 to 0.001 mmol of Al per kg of reactor content. Preference is given to
- 5 using triisobutylaluminum or triethylaluminum in a concentration of from 10 to 0.01 mmol of Al per kg of reactor contents; in this way, a low Al/M<sup>1</sup> molar ratio can be chosen in the synthesis of a supported catalyst system.
- 10 In addition, an additive such as an antistatic can be used in the process of the present invention, e.g. for improving the particle morphology of the polymer.

- It is generally possible to use all antistatics which are
- 15 suitable for polymerization. Examples are salt mixtures of calcium salts of Medialan acid and chromium salts of N-stearyl anthranilic acid as described in DE-A-3,543,360. Further suitable antistatics are, for example, C<sub>12</sub>-C<sub>22</sub>-fatty acid soaps of alkali metals or alkaline earth metals, salts of sulfonic esters,
- 20 esters of polyethylene glycols with fatty acids, polyoxyethylene alkyl ethers, etc. An overview of antistatics is given in EP-A-0,107,127.

- It is also possible to use a mixture of a metal salt of Medialan
- 25 acid, a metal salt of anthranilic acid and a polyamine as antistatic, as described in EP-A-0,636,636.

- Commercially available products such as Stadis<sup>®</sup> 450 from DuPont, namely a mixture of toluene, isopropanol, dodecylbenzenesulfonic
- 30 acid, a polyamine, a copolymer of 1-decene and SO<sub>2</sub> and also 1-decene, or ASA<sup>®</sup>-3 from Shell and ARU5R<sup>®</sup> 163 from ICI can likewise be used.

- The antistatic is preferably used as a solution; in the preferred
- 35 case of Stadis<sup>®</sup> 450, preference is given to using from 1 to 50% by weight of this solution, preferably from 5 to 25% by weight, based on the mass of the support catalyst used (support together with covalently bound metallocenium-forming compound and one or more metallocene compounds, e.g. of the formula IV). However, the
- 40 amount of antistatic required can vary within a wide range, depending on the type of antistatic used.

The following examples illustrate the invention.

- 45 General procedures: Preparation and handling of the compounds were carried out in the absence of air and moisture under argon (Schlenk technique). All solvents required were dried before use

by boiling for a number of hours over suitable desiccants and subsequent distillation under argon. To characterize the compounds, samples were taken from the individual reaction mixtures and dried in an oilpump vacuum.

5

Example 1: Synthesis of bis(pentafluorophenyloxy)methylalane (1)

5.2 ml of trimethylaluminum (2M in Exxol, 10.8 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled to -40°C. 4.0 g (21.6 mmol) of pentafluorophenol in 40 ml of toluene are added dropwise to this solution over a period of 30 minutes. The mixture is stirred for 15 minutes at -40°C and the reaction solution is subsequently allowed to warm to room temperature. It is stirred for another one hour at room temperature. This results in a colorless solution (0.14 M based on Al) of bis(pentafluorophenyloxy)methylalane.

<sup>19</sup>F-NMR (C<sub>6</sub>D<sub>6</sub>): δ = -160.5 ppm (m, 4F, o-C<sub>6</sub>F<sub>5</sub>); -161.8 ppm (m, 2F, p-C<sub>6</sub>F<sub>5</sub>); -166.3 ppm (m, 4F, m-C<sub>6</sub>F<sub>5</sub>).

20

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ = -0.4 ppm (s, 3H, CH<sub>3</sub>).

Example 2: Synthesis of bis(pentafluorophenyloxy)ethylalane (2)

5.0 ml of triethylaluminum (2.1 M in Varsol, 10.5 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled to -40°C. 4.0 g (21.0 mmol) of pentafluorophenol in 40 ml of toluene are added dropwise to this solution over a period of 30 minutes. The mixture is stirred for 15 minutes at -40°C and the reaction solution is subsequently allowed to warm to room temperature. It is stirred for another one hour at room temperature. This results in a colorless solution (0.13 M based on Al) of bis(pentafluorophenyloxy)ethylalane.

<sup>19</sup>F-NMR (C<sub>6</sub>D<sub>6</sub>): δ = -160.9 ppm (m, 4F, o-C<sub>6</sub>F<sub>5</sub>); -162.1 ppm (m, 2F, p-C<sub>6</sub>F<sub>5</sub>); -167.3 ppm (m, 4F, m-C<sub>6</sub>F<sub>5</sub>)

<sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ = 0.5 ppm (t, 3H, CH<sub>3</sub>), 1.6 ppm (q, 2H, CH<sub>2</sub>).

Example 3: Synthesis of bis(pentafluoroanilino)methylalane (3)

5.0 ml of trimethylaluminum (2.1 M in Exxol, 10.5 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled to -40°C. 3.8 g (21.0 mmol) of pentafluoroaniline in 40 ml of toluene are added dropwise to this solution over a period of 30 minutes. The mixture is stirred for 15 minutes at -40°C and the reaction solution is subsequently allowed to warm to room

temperature. It is stirred for another two hours at room temperature. This results in a yellowish solution (0.13 M based on Al) of bis(pentafluoroanilino)methylalane.

5  $^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -162.9$  ppm (m, 4F, o- $\text{C}_6\text{F}_5$ );  $-164.1$  ppm (m, 2F, p- $\text{C}_6\text{F}_5$ );  $-171.3$  ppm (m, 4F, m- $\text{C}_6\text{F}_5$ )

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -0.4$  ppm (t, 3H,  $\text{CH}_3$ ), 5.6 ppm (s, 1H, NH).

10 Example 4: Synthesis of bis(bis(pentafluorophenyl)methoxy)-methylalane (4)

5.0 ml of trimethylaluminum (2.1 M in Exxol, 10.5 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled  
15 to  $-40^\circ\text{C}$ . 7.6 g (21.0 mmol) of bis(pentafluorophenyl) carbinol in 40 ml of toluene are added dropwise to this solution over a period of 30 minutes. The mixture is stirred for 15 minutes at  $-40^\circ\text{C}$  and the reaction solution is subsequently allowed to warm to room temperature. It is stirred for another two hours at room  
20 temperature. This results in a yellowish solution (0.13 M based on Al) of bis(bis(pentafluorophenyl)methoxy)methylalane.

$^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -140.6$  ppm (m, 4F, o- $\text{CH}(\text{C}_6\text{F}_5)_2$ );  $-151.7$  ppm (m, 2F, p- $\text{CH}(\text{C}_6\text{F}_5)_2$ );  $-159.5$  ppm (m, 4F, m- $\text{CH}(\text{C}_6\text{F}_5)_2$ ).

25

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 6.2$  ppm (s, 1H, CH).

Example 5: Synthesis of bis(3,5 bis(trifluoromethyl)anilino)-methylalane (5)

30

5.0 ml of trimethylaluminum (2.1 M in Exxol, 10.5 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled to  $-40^\circ\text{C}$ . 4.8 g (21.0 mmol) of 3,5-bis(trifluoromethyl)aniline in 40 ml of toluene are added dropwise to this solution over a  
35 period of 45 minutes. The mixture is stirred for 15 minutes at  $-40^\circ\text{C}$  and the reaction solution is subsequently allowed to warm to room temperature. It is stirred for another four hours at room temperature. The slightly turbid solution is filtered through a G4 frit. This results in a clear yellowish solution (0.13 M based  
40 on Al) of bis(3,5-bis(trifluoromethyl)anilino)methylalane.

$^{19}\text{F}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = -61.5$  ppm (s, 12F,  $\text{CF}_3$ ).

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 5.5$  ppm (s, 1H, NH), 6.3 ppm (s, 2H, Ar-H), 7.2  
45 ppm (s, 1H, Ar-H).

## Example 6: Synthesis of bis(nonafluorobiphenyloxy)methylalane (6)

5.0 ml of trimethylaluminum (2.1 M in Exxol, 10.5 mmol) together with 40 ml of toluene are placed in a reaction vessel and cooled to -40°C. 7.0 g (21.0 mmol) of nonafluorobiphenyl-1-ol in 40 ml of toluene are added dropwise to this solution over a period of 40 minutes. The mixture is stirred for 30 minutes at -40°C and the reaction solution is subsequently allowed to warm to room temperature. It is stirred for another one hour at room temperature. The slightly turbid solution is filtered through a G4 frit. This results in a clear solution (0.13 M based on Al) of bis(nonafluorobiphenyloxy)methylalane.

19F-NMR ( $C_6D_6$ ):  $\delta$  = -134.0 ppm (m, 2F, 2,2'-F); -137.2 ppm (m, 2F, 3, 3'-F); -154.6 ppm (m, 2F, 4, 4'-F); 157.0 ppm (m, 1F, 6-F); 161.7 (m, 2F, 5, 5'-F).

1H-NMR ( $C_6D_6$ ):  $\delta$  = -0.3 ppm (s, 3H,  $CH_3$ ).

20 General description of the application to a support, the preparation of the catalyst and the polymerization procedure

## A) Application to a support:

25 14.0 g of  $SiO_2$  (XPO 2107, from Grace, dried at 600°C in a stream of argon) together with 20 ml of toluene are placed in a reaction vessel, 2.6 ml of N,N-dimethylaniline (20.80 mmol) are added dropwise and the mixture is stirred at room temperature for two hours. 20.80 mmol of the appropriate cocatalyst, dissolved in 30 40 ml of toluene, are subsequently added at 0°C. The suspension is allowed to warm to room temperature and is stirred for two hours at this temperature. The resulting bluish suspension is filtered and the residue is washed with 50 ml of toluene and then three times with 100 ml each time of n-pentane. The residue is 35 subsequently dried in an oil pump vacuum. This gives the supported cocatalyst system, which is weighed.

## B) Preparation of the catalyst system

40 0.30 ml of trimethylaluminum (20% strength in Exxol, 700  $\mu$ mol) is added to a solution of 50 mg (80  $\mu$ mol) of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride in 50 ml of toluene, and the solution is stirred at RT for 1.5 hours. 960  $\mu$ mol/g of [ $SiO_2$ ] of the cocatalyst prepared 45 under A Application to a support are subsequently added a little at a time. The mixture is stirred at room temperature for 30



minutes. The solvent is then removed in an oil pump vacuum. This gives a light-red free-flowing powder.

#### Example 4

5

#### Polymerization

For introduction into the polymerization system, the appropriate amount of the supported catalyst system (6  $\mu\text{mol}$  of metallocene) prepared under B is resuspended in 30 ml of Exxol.

In parallel thereto, a dry 16 dm<sup>3</sup> reactor is flushed firstly with nitrogen and subsequently with propylene and charged with 10 dm<sup>3</sup> of liquid propene. 0.5 cm<sup>3</sup> of a 20% strength triisobutylaluminum solution in Varsol diluted with 30 cm<sup>3</sup> of Exxol was then introduced into the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently introduced into the reactor. The reaction mixture was heated to the polymerization temperature of 60°C (4°C/min) and the polymerization system was maintained at 60°C for 1 hour by means of cooling. The polymerization was stopped by venting the remaining propylene. The polymer is dried in a vacuum drying oven. The reactor displayed no deposits on the interior wall or stirrer.

25

#### Polymerization results

30	Supported catalyst system prepared from product from Example:	1	2	3	4	5	6
35	Amount of metallocene [mg]	50	50	50	50	50	50
	Metallocene (mmol)	80	80	80	80	80	80
40	Cocatalyst (mmol)	960	960	960	960	960	960
	SiO <sub>2</sub> weighed in [g]	14.0	14.0	14.0	14.0	14.0	14.0
45	SiO <sub>2</sub> weighed out [g]	19.95	19.28	19.46	23.60	21.49	23.49

5	Amount of supported cocatalyst weighed in [mg]	923	1074	1000	1074	893	997
10	Amount of catalyst system weighed out [mg]	975	1124	1050	1124	943	1047
15	Amount of catalyst system weighed in for polymerization [mg] [6 mmol of metallocene]	73	85	79	85	71	79
20	Time (min)	60	60	60	60	60	60
	PP (kg)	0.622	0.480	0.484	0.589	0.281	0.589
	Activity <sup>1)</sup>	166	128	129	157	75	157

25

1) Activity: kg of (PP) / g of metallocene x h

30

35

40

45

00000000 01400

We claim:

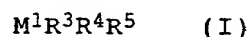
1. A catalyst system comprising

5

A) at least one metallocene,

B) at least one Lewis base of the formula I

10



where

15

$R^3$ ,  $R^4$ ,  $R^5$  are identical or different and are each a hydrogen atom or a  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_6$ - $C_{40}$ -haloaryl,  $C_7$ - $C_{40}$ -alkylaryl or  $C_7$ - $C_{40}$ -arylalkyl group or two or all three of the radicals  $R^3$ ,  $R^4$  and  $R^5$  may be joined to one another via  $C_2$ - $C_{20}$  units,

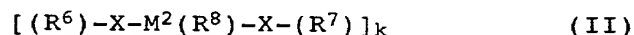
20

$M^1$  is an element of main group V of the Periodic Table of the Elements, in particular nitrogen or phosphorus

C) at least one support

25

D) and at least one organoboron or organoaluminum compound which is made up of units of the formula II



30

where

$R^6$ ,  $R^7$  are identical or different and are each a hydrogen atom, a halogen atom, a boron-free  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl or an  $Si(R^9)_3$  group,

35

where  $R^9$  is a boron-free  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,  $C_6$ - $C_{20}$ -aryl,  $C_6$ - $C_{20}$ -haloaryl,  $C_6$ - $C_{20}$ -aryloxy,  $C_7$ - $C_{40}$ -arylalkyl,  $C_7$ - $C_{40}$ -haloarylalkyl,  $C_7$ - $C_{40}$ -alkylaryl,  $C_7$ - $C_{40}$ -haloalkylaryl,

45

$R^8$  can be identical to or different from  $R^6$  and  $R^7$  and is a hydrogen atom, a halogen atom, a  $C_1$ - $C_{40}$  group such as  $C_1$ - $C_{20}$ -alkyl,  $C_1$ - $C_{20}$ -haloalkyl,  $C_1$ - $C_{10}$ -alkoxy,

## 60

C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>6</sub>-C<sub>20</sub>-haloaryl, C<sub>6</sub>-C<sub>20</sub>-aryloxy,  
 C<sub>7</sub>-C<sub>40</sub>-arylalkyl, C<sub>7</sub>-C<sub>40</sub>-haloarylalkyl,  
 C<sub>7</sub>-C<sub>40</sub>-alkylaryl, C<sub>7</sub>-C<sub>40</sub>-haloalkylaryl or an OSi(R<sup>9</sup>)<sub>3</sub>  
 group,

5

X may be identical or different and are each an element  
 of group V or VIa of the Periodic Table of the  
 Elements or an NH group,

10

M<sup>2</sup> is an element of group IIIa of the Periodic Table of  
 the Elements and

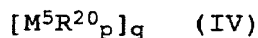
k is a natural number from 1 to 100,

15

and is covalently bound to the support.

2. A catalyst system as claimed in claim 1 which further  
 comprises an organometallic compound of the formula (IV)

20



where

25

M<sup>5</sup> is an element of main group I, II or III of the  
 Periodic Table of the Elements, preferably lithium,  
 magnesium or aluminum, in particular aluminum,

30

R<sup>20</sup> are identical or different and are each a hydrogen  
 atom, a halogen atom or a C<sub>1</sub>-C<sub>40</sub> group such as  
 C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>6</sub>-C<sub>40</sub>-aryl, C<sub>7</sub>-C<sub>40</sub>-arylalkyl or  
 C<sub>7</sub>-C<sub>40</sub>-alkylaryl,

p is an integer from 1 to 3 and

35

q is an integer from 1 to 4.

40

3. A process for preparing a polyolefin by polymerization of one  
 or more olefins in the presence of a catalyst system as  
 claimed in claim 1 or 2.

4. The use of a catalyst system as claimed in claim 1 or 2 for  
 preparing a polyolefin.

45

COMBINED DECLARATION AND POWER OF ATTORNEY

Attorney Docket No.  
Basell-5 (9086\*179)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

CATALYST SYSTEM

the specification of which

(check one) ☐ is attached hereto.

☐ was filed as PCT international application Number PCT/EP00/03263 on 12 April 2000 ..

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, ' 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. ' 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or ' 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>199 17 985.9</u>	<u>Germany</u>	<u>21 April 1999</u>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	No	yes
<u>                    </u>	<u>                    </u>	<u>                    </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	No	yes
No				

I hereby claim the benefit under 35 U.S.C. ' 119(e) of any United States provisional application(s) listed below.

                                           
(Application No ) (filing date)

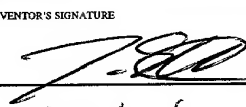
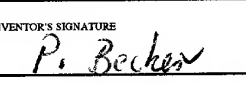
I hereby claim the benefit under Title 35, United States Code, ' 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, ' 112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, ' 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

<u>PCT/EP00/03263</u>	<u>12 April 2000</u>	<u>Published (WO 00/62928)</u>
(Application Serial No.)	(Filing Date)	(Status)
<u>                    </u>	<u>                    </u>	<u>                    </u>
(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

In the matter of the above-identified application, please recognize the attorneys associated with CUSTOMER NUMBER 23416; all of CONNOLLY BOVE LODGE & HUTZ LLP, as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

Send Correspondence To: <b>Connolly Bove Lodge &amp; Hutz LLP</b> P.O. Box 2207 Wilmington, Delaware 19899-2207		Direct Telephone Calls To:  (302) 658-9141	
FULL NAME OF SOLE OR FIRST INVENTOR <b>Jörg Schottek</b>		INVENTOR'S SIGNATURE 	DATE September 20, 2001
RESIDENCE Mühlgasse 3, 60486 Frankfurt, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Same as residence			
FULL NAME OF SECOND JOINT INVENTOR IF ANY <b>Patricia Becker</b>		INVENTOR'S SIGNATURE 	DATE September 20, 2001
RESIDENCE Alpenring 39, 64546 Mörfelden-Walldorf		CITIZENSHIP German	
POST OFFICE ADDRESS Same as Residence			
FULL NAME OF THIRD JOINT INVENTOR IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FOURTH JOINT INVENTOR IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH JOINT INVENTOR IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH JOINT INVENTOR IF ANY		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			

168908